RAYLO CHEMICALS LIMITED
Subsidiary of Terochem Laboratories Limited
8045 Argyll Road, Edmonton, Alberta, Canada T6C 4A9
Telephone (403) 465-7937 Telex 037-43236

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QUANTITATIVE ANALYSIS OF COAL IN THE PRESENCE OF COKE USING FOURIER TRANSFORM INFRARED SPECTROSCOPY

FINAL REPORT

BY

RAYLO CHEMICALS LIMITED

Work on this project was conducted under the auspices of the Energy Research Laboratories, Department of Energy, Mines and Resources, CANMET.

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SUMMARY

Reference samples of low temperature ash and of the tetrahydrofuran insoluble components of altered Athabasca subbituminous coal, bitumen coke, coal derived liquids coke and a bitumen-coal coprocessing residue were prepared.

FTIR spectra, normalized to one milligram sample in 300 milligrams potassium bromide (KBr) were obtained. The spectra of the samples varied with each KBr disc prepared. The variations could be smoothed out by averaging the spectra but different averaging methods gave slightly different results.

Quantitative ash determination by subtraction of the ash spectrum from the spectra of those materials containing ash met with modest success. Slight shifts in the position of the ash absorbance bands in the spectra of different samples made the judgement of the correct degree of subtraction very subjective.

Subtraction of the altered coal or coke spectra from the spectrum of the coprocessing residue lead to a difference spectrum which did not resemble the spectra of any of the reference materials. Attempts to synthesize a coprocessing residue spectrum from the spectra of the reference materials led to indifferent results.

Subtraction of the altered coal spectrum from the spectrum of a tetrahydrofuran extracted CANMET coprocessing residue lead to the conclusion that the CANMET residue did not contain any material which resembles altered coal.

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I. INTRODUCTION

This contract is based on a concept proposed by Rayio in response to an analytical problem that the Energy Research Laboratories (ERL) had in interpreting the results of coprocessing coal and bitumen. The concept was refined in subsequent discussions between Rayio and ERL. Energy Research Laboratories of CANMET placed this contract with Rayio and the contract was issued by DSS on November 4, 1982 and was to run through February 28, 1983.

II. BACKGROUND

On coprocessing mixtures of heavy oil (bitumen) and coal, a solid residue is obtained as a by-product. This residue consists of mineral matter, unreacted coal and coke. The coke is produced by partial carbonization of bitumen, coal and coal derived liquids. In order to evaluate the coal conversion in the process, a quantitative evaluation of unreacted coal in the solid residue is essential.

Currently, the amount of unreacted coal in the residue is estimated in a complex and unreliable manner. In parallel experiments, the amount of coke produced from bitumen and the amount of coal residue formed under the same processing conditions (temperature and pressure) in a non-coking solvent (hydrogenated anthracene oil) are measured. In the final calculation, the amount of coke expected from the bitumen run is subtracted from the total residue obtained in a coprocessing experiment, involving both heavy oil and coal, to estimate the quantity of altered coal.

An analytical method is required to determine the composition of the sample rapidly and reproducibly. On the basis of the literature information, it appeared that Fourier transform infrared (FTIR) spectroscopy offered a basis for the development of the required analytical method.

FTIR has significant advantages over dispersion ir in several ways relevant to this problem. Spectra can be accumulated from multiple scans which makes it possible to obtain good spectra of strongly absorbing compounds. The other advantages lie in the area of data handling. Spectra can be normalized to a standard amount of material which makes the absorption measurements quantitative. Using the normalized spectra of the standards and the sample, it is possible to add or subtract spectra and so determine quantitatively the composition of a mixture. In particular, the literature implies that it should be possible to subtract the spectrum of the ash from the spectrum of the residual coal and coke mixture and then operate on an ash free basis. If the spectrum of coke produced from coal, or coal derived liquids, is different from the spectrum of coke produced from the bitumen, it should be possible to measure the quantities of residual coal and of each coke present in a mixture.

The literature documents a modest body of work in which the above techniques have been applied (1,2). It is significant to note, however, that the quantitative determination of components in a coal derived mixture by the subtraction technique has been reported only for the determination of specific clays in the ash component. Subtraction

was not always straight forward and it had been observed that slight shifts in the absorbance bands in the spectra of the reference materials lead to erroneous results (3,4).

III. RESULTS AND DISCUSSION

A. Starting Material Description

The starting material provided by the Energy Mines and Resources Laboratories were six litres of anthracene oil, six litres of Cold Lake vacuum bottoms (CLVB) and six kilograms of 200 to 400 mesh Athabasca subbituminous coal impregnated with 10% $FeSO_4$. The analysis of the coal is summarized in Table I.

B. Preparation of Samples for FTIR

1. Low Temperature Ash

A thin layer of coal was spread along the bottom of a porcelain container and heated in a muffle furnace to 600°C at a rate of 10° per minute. The temperature was held at 600° for one hour, then increased to 750° at a rate of 2.5° per minute and held for one hour. The ash was cooled under vacuum. In duplicate runs, the yield of ash was 10.0% and 11.0% which agrees well with the proximate analysis (10.5%). The average normalized FTIR spectrum of low temperature ash is shown in Figure 1.

2. Altered Coal

a) Coal altered in the presence of anthracene oil

The supplied coal (15 grams) and 45 grams anthracene oil were placed in a 150 ml autoclave which has design specifications of 6000

psig at 600°C. The autoclave was protected by a bursting disc and attached to a manifold which has provision for a pressure gauge (5000 psi) and two high pressure valves. One of the valves was connected to a water aspirator while the other valve was connected to a hydrogen cylinder. The autoclave was evacuated, then pressurized with 1800 psig hydrogen at ambient temperature. The autoclave was heated to 450° using a fluidized sand bath. The heat-up time was about 1.5 hours. The temperature was held at 450° for one hour. The autoclave was then cooled to room temperature and the pressure released. The autoclave was opened and the contents transferred to a Soxhlet thimble and extracted for 24 hours with tetrahydrofuran (THF) in a Soxhlet extractor. The thimble residue was dried in a vacuum desiccator to leave 9 grams of altered coal. This and similar experiments are summarized in Table II. The averaged normalized FTIR spectrum of this material is shown in Figure 2. The hydrogen to carbon ratio was 0.45 (5).

b) Coal altered in the presence of toluene

The above procedure was repeated using 15 grams of coal and 45 grams of toluene. The residue, after THF extraction weighed 7.1 grams (Table II). The averaged normalized FTIR spectrum of this material is reproduced in Figure 3. The carbon to hydrogen ratio was 0.56 (5).

c) Coal altered in the absence of solvent

Coal (25 grams) was heated in a hydrogen atmosphere as described above. The residue remaining after THF extraction weighed 10.2 grams (Table II). The averaged normalized FTIR spectrum is reproduced in Figure 4 and the hydrogen to carbon ratio was 0.56 (5).

3. Coke from Cold Lake Vacuum Bottoms (CLVB)

CLVB (29.3 grams) was placed in the autoclave and treated as described above. The pressure increase with temperature increase closely followed the ideal gas laws up to 370°. The pressure increase was more rapid from 370 to 450° than could be accounted for by the temperature increase alone implying that coking of CLVB starts at 370° resulting in the release of gaseous materials. The final products were a very mobile liquid and a hard carbonaceous material. The solids were extracted with THF for 24 hours to leave 7.6 grams (25.9%) bitumen coke (Table II). The averaged normalized FTIR spectrum of this material is shown in Figure 5.

In a separate experiment, CLVB was found to be completely soluble in THF.

4. Coke From Coal Derived Liquids

Coal derived liquids (cdl) obtained from Forestburg subbituminous coal by supercritical toluene extraction was rendered process solvent free by heating to 200° at atmospheric pressure. The solvent free cdl (37.4 grams) was transferred to the reaction autoclave and treated as described above. The residue, after THF extraction weighed 12.0 grams (Table II). The averaged normalized FTIR spectrum is shown in Figure 6.

5. Coprocessing Residue

A mixture of Athabasca subbituminous coal (10 grams) and CLVB (30 grams) was treated as described above. The solid residue remaining after THF extraction was 13.3 grams (33.3%). Figure 7 shows the averaged normalized FTIR spectrum of the coprocessing residue.

6. Summary

A number of the above experiments were duplicated using the same ratios but different amounts of materials to ensure that the amounts of residue isolated were representative.

C. Potassium Bromide Disc Preparation and Spectral Normalization

The solid residues obtained above were ground in a mortar to breakup any agglomeration. This action produced a finely divided solid which could readily pass through a 100 mesh screen.

1. Disc Preparation and Normalization Procedure

The potassium bromide (KBr) disc preparation method followed has been described by Painter (6).

The KBr disc of the samples were prepared by grinding a one milligram (accurately weighed) sample with 300 milligrams (accurately weighed) KBr in a Perkin-Elmer Wig-L-Bug for a total of 30 minutes using ten minutes grinding time, a break followed by a further ten minutes grinding time etc. The entire sample was transferred and the disc was prepared by pressing at 20,000 psi for three minutes. The disc was then reweighed. The final weight of sample in the disc was calculated using the formula:

$$w = xy/z$$

where w = final weight of sample in disc

x = initial weight of sample (about 1 mg)

y = weight of KBr disc (usually less than 300 mg)

z = initial weight of KBr (about 300 mg)

The disc was then kept overnight in a desiccator before the spectrum was obtained.

Spectra to be used for quantitative determinations were normalized to one milligram by multiplying the spectra by a factor of 1/w. An actual example for bitumen coke follows.

sample weighed x = 1.152 mg

KBr weighed z = 299.9 mg

Weight disc y = 284.3

$$w = \frac{1.152 \times 284.3}{299.9} = 1.0921$$

$$1/w = 0.9157$$

2. Instrumentation

Spectra were obtained using a Nicolet 7199 Fourier Transform Infrared instrument. This spectrophotometer comes complete with the Nicolet 1180 computer. The spectra were obtained using 50 scans at 4 cm^{-1} resolution.

D. FTIR Spectra Acquisition

1. Reproducibility of the Average Spectral Strength

The computer associated with the FTIR instrument is capable of adding, subtracting, averaging and curve fitting. Normalized spectra may be subtracted from each other to obtain a quantitative result. The subtraction technique is useful for determining the reproducibility of spectra obtained from the same sample of a complex material. This is illustrated in Figures 8 and 9. Figure 8 shows the averaged normalized spectrum of ash (Figure 1) and the spectrum obtained by regrinding the individual KBr discs (see below) and forming a new disc. The spectra

are very similar with perhaps a slightly better degree of resolution obtained for the reground disc. If the spectra were identical, subtraction of one from the other would result in a flat baseline. However, one spectrum is slightly "stronger" in certain absorbance regions while the other is somewhat "stronger" in other absorbance regions. In order to get the indicated baseline, the computer multiplies the spectrum with the stronger overall absorbance by a factor of less than one (0.9466 in this case) to make the stronger spectrum equal to the weaker spectrum before subtracting. In this case, the spectrum of the material obtained by regrinding the ash discs is about 95% as strong as the averaged normalized reference spectrum. The difference can probably be attributed to losses on regrinding. Note that only the absorbance range of 540 to 1233 cm^{-1} is reproduced in this figure.

Figure 9 shows two normalized spectra of coal altered in the absence of solvent. The averaging of these two spectra (see below) produces the averaged normalized FTIR reference spectrum reproduced in Figure 4. Note that one spectrum shows generally much stronger absorbance throughout the range even though both spectra are normalized to one milligram of sample per disc. In this case the computer needed to multiply the stronger spectrum by a factor of 0.661 before subtraction in order to produce the best zero baseline. This would imply that one spectrum was obtained from only 66% as much material as the other spectrum. The cause of this large discrepancy is not apparent. This was, however, a commonly observed phenonenom and is one

large factor making the results obtained by quantitative manipulation of the FTIR spectra suspect.

2. Reproducibility of the Absorption Bands

Three KBr discs were prepared as described above for each of the reference materials. Figure 10 shows the normalized spectra, before baseline correction, for altered coal. The curves numbered 1, 2 and 3 are obtained for the individual discs prepared from the sample. The three curves show significant differences. For example, in curve 1 the baseline is "pushed up" in the 400 - 700 cm^{-1} region, in curve 2 the baseline is "pushed up" in the 700 - 950 cm^{-1} region while for curve 3 the baseline is "pushed up" over the entire 400 to 900 cm^{-1} region. Similarly, both the position and the absorbance of the absorption peaks differ quite significantly in the 1000 - 2000 cm^{-1} region. The absorbance shift is illustrated by the absorbance bands in the 1150 to 1160 cm^{-1} region and the 1600 cm^{-1} region as summarized in the following Table.

Wave numbers of absorbances in the 1160 and 1600 cm^{-1} regions of altered coal.

Spectrum 1	Spectrum 2	Spectrum 3
1158	1152	1155
1620	1602	1605

The absorbance at about 1600 cm^{-1} is common to all coal and coke products and is due to hydroxyl enhanced aromatic stretch. Qualitatively, the stronger the absorbance at 3420 cm^{-1} (water), the greater the upward shift of the 1600 cm^{-1} absorbance. Also noteworthy is the absorbance ratio of the aliphatic C-H stretch (2810 - 2990 cm^{-1}) to the aromatic C-H stretch (3025 cm^{-1}) which is about the same in curves 1 and 3 but is much larger in curve 2.

Similar variations were detected in all the spectra taken of the reference materials. It is not known if the source of the spectral variations are due to the heterogeneity of the materials and therefore real or are a result of sample handling techniques.

3. Reference Spectra by Averaging

Since three KBr dics prepared from the same sample resulted in three different spectra, it was impossible to determine which spectrum was representative of the sample. It seemed prudent, therefore, to generate representative spectra by averaging a number of individual spectra.

There are several ways in which spectra can be averaged and Figures 10 and 11 show the results of various averaging methods. Curve 1, Figure 11, was obtained by applying a "baseline correct" method to each of the individual spectra shown in Figure 10, then applying a coaddition program supplied by the instrument manufacturer. This program utilized only 112 of the total of 150 interferograms to obtain the average spectrum. Curve 2, Figure 11, was obtained by using the coaddition program before correcting for baseline drift. Again only

112 of the 150 interferograms were used to obtain the spectrum. Curve 3, Figure 11, was obtained by multiplying each of the three spectra in Figure 10 by 0.33333, followed by addition then followed by baseline correct. Curve 3, Figure 13, is equivalent to Figure 2.

Inspection of the spectra in Figure 11 shows that curves 1 and 2 are qualitatively the same. The absolute absorbance of the various absorbance bands are greater in curve 1 than in curve 2 in the 400 to 1700 cm^{-1} region but smaller in the 1700 to 4000 cm^{-1} region. This indicates that the time at which a baseline correct is applied, before or after averaging, has an effect on the resultant spectrum. Curve 3 shows a lower absorbance for all the bands relative to curves 1 and 2. The absorbance ratio of some of the peaks varies as well. This is clearly illustrated by the paired peaks at 600 cm^{-1} and 815 cm^{-1}.

Utilizing all the raw spectral data is the most satisfactory means of obtaining a "representative" spectrum of the reference material. This method was used to obtain the averaged normalized spectra of each of the individual reference samples (Figures 1 through 7).

4. Spectral Subtraction

With averaged normalized spectra of the reference samples in hand, it should have been possible to quantitatively subtract the reference spectrum from the mixture spectrum to determine the absolute amount of that reference material in the mixture.

a) Subtraction of a simple contaminant from bitumen coke

In a number of early spectra of the solid residues, an absorbance band in the 1700 cm^{-1} region had apparently developed after the material had stood in a normally capped vial for one month. Oxidation of the sample was thought to be a possible cause for this band. It was found, however, that the samples had been inadvertantly contaminated with acetone during the preparation of the KBr discs and the absorbance at 1700 cm^{-1} is due to the acetone carbonyl. Figure 12 shows the spectrum of acetone incorporated in a KBr disc. Figure 13 shows the spectrum of bitumen coke contaminated with acetone. The absorbances due to acetone are marked with arrows. Preparation of new KBr discs of bitumen coke, taking care to exclude acetone contamination, did not show any absorbances in the carbonyl region.

With the capability of FTIR instrumentation to subtract spectra, contamination by a known compound should not present a great difficulty since the spectrum of the known contaminant could simply be subtracted to leave the spectrum of the desired material. In practice, this was not possible. Comparison of the acetone absorbance in Figures 12 and 13 immediately demonstrates one of the difficulties encountered in attempting subtractions. The acetone absorbances in the presence of coke are all shifted to lower wave number relative to acetone by itself as summarized in the following Table.

Wave numbers of absorbances due to acetone:

Pure	Mixed with Bitumen Coke
1714	1710
1362	1360
1221	1218
1092	1090
531	531

The shift ranging from 0 to 4 wave numbers is enough to make spectral subtraction meaningless.

b) Subtraction of ash from altered coal

Figure 14 shows the subtraction of ash from altered coal using the disappearance of two characteristic ash absorbances at 596 and 607 cm^{-1} (Figure 1) to determine the degree of subtraction required. The result was that the normalized ash spectrum had to be multiplied by a factor of 0.122 followed by subtraction from Figure 2 to leave Figure 14. The indicated characteristic ash absorbances have disappeared.

The amount of ash in the altered coal can be calculated from the ash content of the initial coal. Ash content of the original coal by proximate analysis was 10.5%. Twenty grams of coal heated with anthracene oil resulted in 12 grams of residue which should contain all the ash initially present. Therefore the ash content of the altered coal will be 17.5%. The spectral subtraction indicates 12.2% ash. The agreement between the two values is not good but appears to be only slightly outside the limits of 3 to 4 percentage points reported by Painter (6) for determining the ratio of clays in an ash.

c) Subtraction of ash from the coprocessing residue

Similar success cannot be reported for the subtraction of ash from the coal-bitumen coprocessing sample (Figure 15). The expected ash content calculated from proximate analysis and the weight of the residue is 7.5%. The amount actually found by low temperature ashing was 7.8%. The amount estimated by spectral subtraction is less than 2%. In this case, the characteristic ash peaks could not be subtracted without immediately forming negative peaks. This is dramatically emphasized in Figure 16 where 7.5% of the ash spectrum is subtracted. The strong absorbance at 1160 cm^{-1} in Figure 1 appears as a strong negative peak in Figure 16. Although the actual error is not much different than for the previous example, the value of the result is questionable.

These puzzling results required further study. Figure 17 shows the spectrum which results when 4.8% of the average normalized ash spectrum was subtracted from a normalized coprocessing spectrum obtained from a single disc. This spectrum was one of the component spectra which makes up the averaged normalized spectrum of the coprocessing residue (Figure 7). In this case the starred ash absorbances do appear to be slightly negative. This result gave encouragement to produce a new averaged normalized spectrum for the coprocessing residue.

Three new KBr discs were prepared by carefully grinding the coprocessing residue with the KBr in a mortar. The three normalized spectra obtained, before correcting for baseline drift and before expanding the absorbance scale, are shown in Figure 18. Inspection of Figure 18 shows that each disc resulted in nearly identical spectra. The water absorbance is nearly the same for all three spectra and very little if any shift in the 1600 cm^{-1} absorbance is noted. These three spectra were averaged, the baseline corrected and the absorbance scale expanded to give Figure 19. Comparison of Figure 19 with Figure 7 shows that Figure 19 has better resolution. Both figures show absorbance envelopes between 900 - 1220 cm^{-1} and 1200 - 1500 cm^{-1}. The ratio of these absorbance envelopes to each other is much closer to one in Figure 19 than they are in Figure 7. Subtraction of the ash spectrum (Figure 1) from Figure 19 lead to the conclusion that the coprocessing residue contains 4.0% ash. This compares reasonably well with the actual ash content of 7.8% found by low temperature ashing.

These observations and results indicate that some of the difficulties encountered in the acquisition and manipulation of spectral data are due to inadequate grinding of the solid residue with the potassium bromide prior to disc preparation. Nevertheless, the observation that ash content determined by FTIR techniques was significantly lower than the actual content in all cases, suggest that there may be a fundamental difficulty with the spectral techniques.

d) Complex spectral subtraction

More compex subtractions were attempted. Figure 20 shows the subtraction of 13% of the spectrum of altered coal from the spectrum of the coprocessing residue. This was the amount that could be subtracted before negative absorbance bands started to appear in the difference spectrum. The residual spectrum does not resemble the spectrum of either of the standard cokes. Similiarly Figure 21 shows the subtraction of 24% of the spectrum of bitumen coke from the spectrum of the coprocessing residue. The residual spectrum also does not bear any resemblance to the spectrum of either the coal derived liquid coke or the altered coal.

5. Synthesis of Spectra

Since the spectral subtraction routine lead to disappointing results, a brief study was launched with the aim of synthesizing coprocessing residue spectra from the spectra of the reference materials. Figure 22 shows the spectrum which results when 25% of the altered coal spectrum (Figure 2) is added to 75% of the bitumen coke spectrum (Figure 5). This ratio was chosen since coal and bitumen are mixed in this ratio before the coprocessing reaction was carried out (Table II).

Figure 23 shows the spectrum obtained from a physical mixture consisting of 25% altered coal and 75% bitumen coke. The spectra in Figure 23 were obtained from separate KBr dics prepared by carefully grinding the solid with potassium bromide in a mortar.

Comparison of Figure 22 and 23 shows that the computer synthesized spectrum and the spectra of the physical mixture contain the same absorbance bands. However, the ratios of the absorbance bands (see for example the C-H absorbance in the 2800 to 3100 cm^{-1} region) and, in some instances, the position of the absorbance bands are different. The shift in absorbance bands is reminiscent of shifts encountered in the spectra involving acetone. The time constraints of this contract precluded any further investigation of this method.

IV. OBSERVATIONS AND CONCLUSIONS

A. Standard Materials

A major consideration in the development of any analytical method is the preparation of proper reference materials. Reference samples of altered coal and coke were obtained by separately subjecting the coal and the bitumen to the coprocessing conditions. The coal was heated in the presence of anthracene oil to prepare a reference altered coal sample. The legitimate question that can be raised is does the coal react in the same way in the presence of anthracene oil, a non-coking solvent, as it does in the presence of bitumen, a coking solvent? To determine what effect the processing environment has on the residue, coal was heated in the presence of toluene and hydrogen and also in the absence of any solvent but in the presence of hydrogen. The FTIR spectra of the residues are reproduced in Figures 3 and 4. Superficial comparison with the spectrum in Figure 2 show that the residues are different. Moreover, the hydrogen to carbon ratio for the coal altered

in anthracene oil (0.45) was substantially different from the ratio obtained for the other two residues (0.56) (5). These observations may help to explain why subtraction of altered coal from a coprocessing residue leaves a spectrum which is different from any of the other reference materials.

B. Representative Spectra

Three types of variability were encountered in obtaining FTIR spectra.

The average intensity of the spectra ranged from disc to disc prepared from the same sample. This was probably random error and could be reduced by improving the definition of the disc preparation method and by averaging.

The positions of the spectral absorption bands and their relative intensities ranged from disc to disc prepared from the same sample. These errors may be due to sample inhomogeneity possibly compounded by inadvertent variations in the disc preparation method. Averaging the spectra leads to loss of resolution.

The position of the absorbances of spectra of standard materials shift slightly when the materials are physically mixed with other materials. These shifts seem to be real effects.

C. Spectral Characteristics of the Reference Materials

The averaged spectra of the reference materials altered coal, bitumen coke and cdl coke as well as the spectrum of the coprocessing residue, are all distinctly different. The difference in the spectrum

of the bitumen coke and the cdi coke in the 1000 to 3000 cm^{-1} region is almost startling. Yet all the spectra are also very similar in that no single absorbance band is characteristic of any of these materials.

D. Spectral Manipulations

Both spectral subtraction and curve fitting depend on the quality of the spectra of reference materials and on the constancy of the position of the absorption peaks. The variation of the position of an absorption peak in mixtures invalidated to a greater or lesser degree the spectral manipulations. Although acknowledged in the literature, the effect of this variability on the manipulation of spectra of complex mixtures is grossly underestimated.

1. Subtraction

The absence of absorbance bands specific to a sample, makes the correct degree of subtraction of a reference spectrum from a mixture spectrum highly subjective. Spectral shifts make many subtractions invalid.

2. Curve Fitting

The synthesis of the spectrum of a mixture by adding the spectra of the components gave a different spectrum (absorption peak shifts) than the spectrum obtained from a physical mixture of the components.

E. Overall Conclusions

1. Well resolved distinct spectra of coal derived products can be obtained by FTIR.

2. The coal derived products can be clearly distinguished from each other by these spectra.
3. With the exception of the ash, the spectra of the coal derived products all contain the same absorption peaks although the relative intensities vary from product to product.
4. The absence of absorbtion peaks specific to each coal derived product makes attempted spectral subtractions subjective.
5. Slight shifting of the absorption peaks in the spectra of physical mixtures make many attempted spectral subtractions or additions invalid.
6. Estimates of the composition of a mixture of components, which are themselves complex mixtures, are at best semi-quantitative.

V. CANMET Samples

The scientific authority, Dr. P. Rahimi, sent 24 samples of coprocessing residues for analysis by FTIR spectroscopy. These samples differed substantially from the reference materials produced in this contract in that none of the samples had been extracted with THF. The samples were either viscous liquids or solids.

A. Liquid Samples

The samples that were in a liquid state were dissolved in THF and the solution cast on a potassium bromide plate, the THF was removed by placing the plate in a dessiccator leaving a thin layer of sample on the plate. The FTIR spectra for these samples were obtained. These spectra are not normalized since THF casts cannot be normalized. The spectra of these samples, identified by their CANMET numbers, are included with the original copy of this report.

B. Solid Samples

Potassium bromide discs were prepared for the solid residues and the normalized FTIR spectra, identified by the CANMET numbers of the sample, are also included with the original copy of this report.

In an attempt to determine the possible amount of altered coal in the solid residues, the spectrum of altered coal (Figure 2) was subtracted from the spectra of the CANMET samples using the disappearence of the ash absorbance bands at 600, 615 and 675 cm^{-1} to determine the correct degree of subtraction. The spectra of the CANMET samples chosen are shown in Figures 24, 25 and 26 and the difference spectra are shown in Figures 27, 28 and 29. The apparent amount of altered coal in the three samples are tabulated below.

Apparent amount of altered coal in CANMET coprocessing residues determined by spectral subtraction.

CANMET Sample	Sample FTIR (Figure)	% Altered Coal	Difference FTIR (Figure)
190582	24	39.8	27
140682	25	43.7	28
010682	26	40.6	29

These results imply that each of the selected samples contains about 40% altered coal and ash, the remainder being coke and THF soluble material.

C. THF Extraction of CANMET Sample 140682

In order to test the validity of the answers obtained above, CANMET sample 140682 (4.0 grams) was extracted for 16 hours with THF in a Soxhlet extractor. The solid residue left in the thimble weighed, upon drying, 0.4 gram (10%). The THF was removed from the extract by rotary evaporation to leave 3.1 grams (77.5%) of THF soluble material. The total recovery from the extraction was 87.5%

The FTIR subtraction routine had suggested that 40% or 1.75 grams of the residue was altered coal, a THF insoluble material. The extraction result totally invalidates the FTIR subtraction results.

A normalized FTIR was taken of the residue remaining after THF extraction (sample number 140682-X; Figure 30). An attempt was made to subtract the altered coal spectrum from the spectrum of 140682-X using the disappearance of the ash absorbances to determine the correct degree of subtraction. However a negative spectrum appeared immediately on subtraction. Taking the ash absorbance bands to baseline resulted in a negative spectrum which is nearly identical to the percent transmittance spectrum of altered coal (Figure 31). These results imply that the THF extracted residue, 140682-X, does not contain any material equivalent to the altered coal reference sample, and consequently CANMET sample 140682 does not contain any of this material.

The ash content of 140682-X was determined by subtraction of the averaged normalized ash spectrum from the normalized spectrum of 140682-X (Figure 32). The ash content was found to be 51.25% by FTIR. Low temperature ashing resulted in an ash content of 55.32%. The correlation in this instance is very good.

To round out this portion of the study, the normalized spectrum of sample 140682-X was subtracted from the normalized spectrum of sample 140682 using the ash absorbances to determine the correct degree of subtraction. The resultant spectrum is reproduced in Figure 33 and should be the spectrum of the THF extracted material. The spectrum of the THF extracted material is reproduced in Figure 34. Inspection of the two spectra show that all the absorbance bands in Figure 33 also appear in Figure 34. Unfortunately, the THF extract appears to be contaminated with a carbonyl containing compound. The contaminant was probably introduced during the extraction procedure since there was no evidence of a carbonyl containing material in the spectrum of the precursor.

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TABLE I

Analysis of the Athabasca Subbituminous Coal Impregnated with 10% $FeSO_4$ supplied by the Energy Research Laboratories, CANMET.

	Analysis by CANMET	Proximate[a)] Analysis	Ultimate[a,b)] Analysis
% Moisture	13.32	15.6	--
% Ash[c)]	14.6	10.5	12.41
% Volatile Matter	--	35.2	--
% Fixed Carbon	--	38.7	--
% C	--	--	60.33
% H	--	--	3.92
% N	--	--	1.33
% S	--	--	1.86
% O[d)]	--	-	20.15
H/C	--	--	0.78

a) Carried out by Chemical and Geological Laboratories Ltd., Edmonton.

b) Dry basis, hydrogen and oxygen from water are not included.

c) Low temperature ashing lead to results of 10.0 and 11.0%.

d) By difference.

TABLE II

Preparation of Reference Samples of Altered Coal, Bitumen Coke and Coal Derived Liquids Coke.

Material (g)	Solvent (g)	THF Insoluble Grams	Residue % of Initial Charge
Coal[a] (15)	Anthracene Oil (45)	9.0	15.0
Coal (20)	Anthracene Oil (60)	12.0	15.0
Coal (15)	Toluene (45)	7.1	11.8
Coal (25)	Neat	10.2	40.8
CLVB[b] (29.3)	Neat	7.6	25.9
CLVB (80)	Neat	20.8	26.0
CDL[c] (37.4)	Neat	12.0	32.1
Coal (10)	CLVB (30)	13.3	33.3

a) Athabasca subbituminous coal impregnated with 10% ferrous sulfate supplied by CANMET.

b) Cold Lake vacuum bottoms.

c) Coal derived liquids obtained by supercritical toluene extraction of Forestburg subbituminous coal.

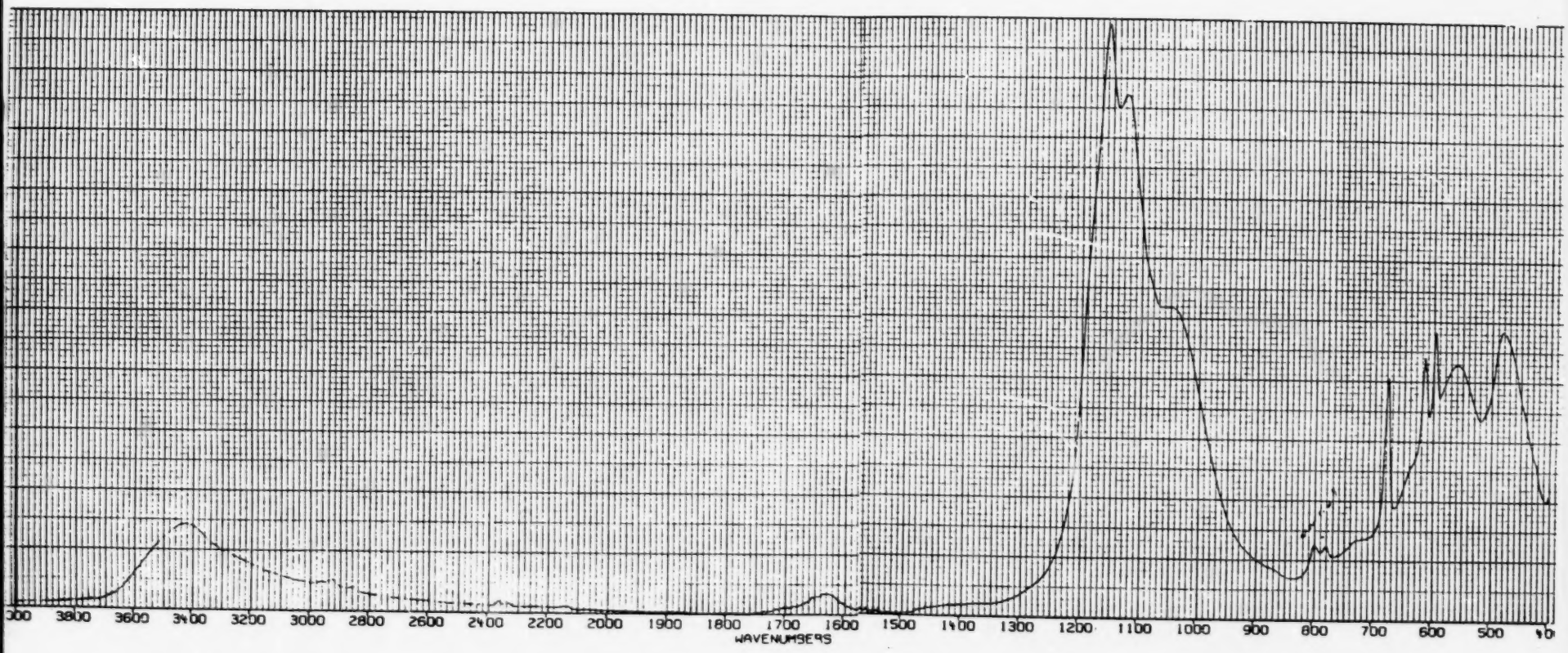

Figure 1: Averaged normalized FTIR spectrum of low temperature ash.

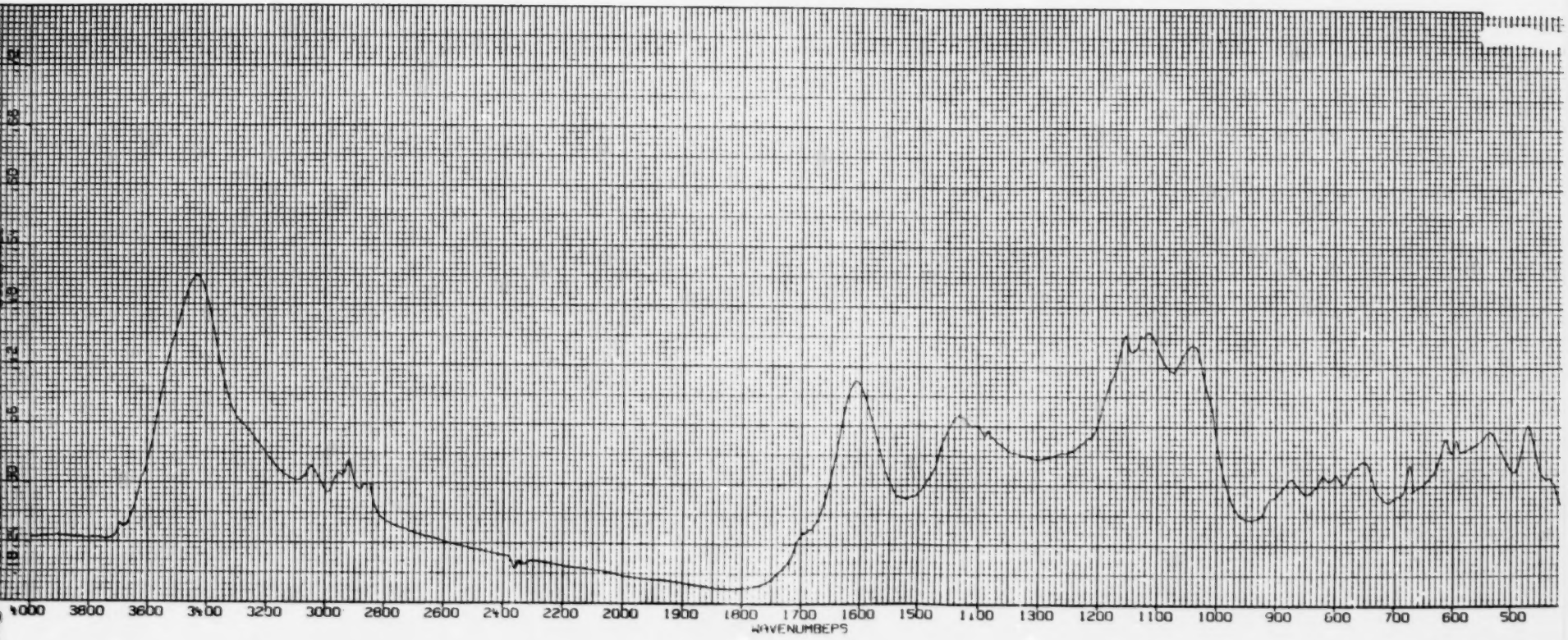

Figure 2: Average normalized FTIR spectrum of coal altered in the presence of anthracene oil.

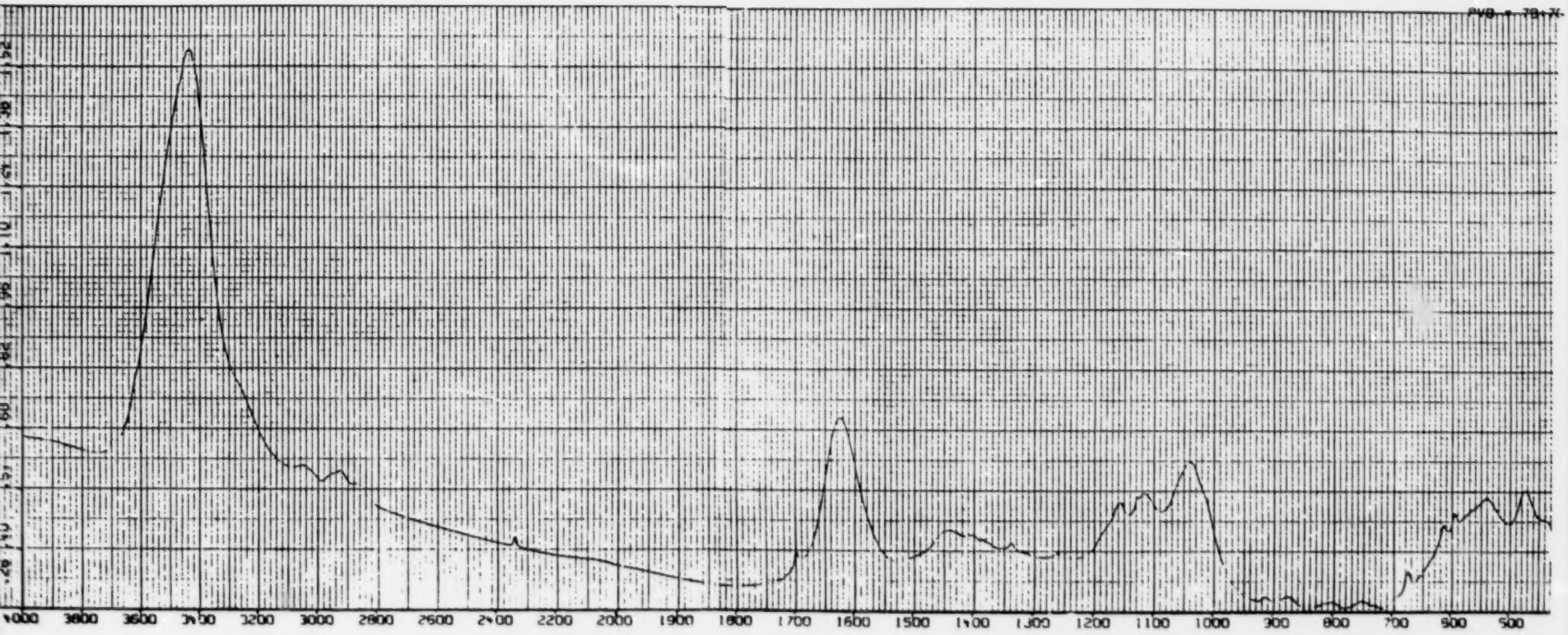

Figure 3: Averaged normalized spectrum of coal residue remaining after heating coal at 450°C for one hour in the presence of toluene and hydrogen.

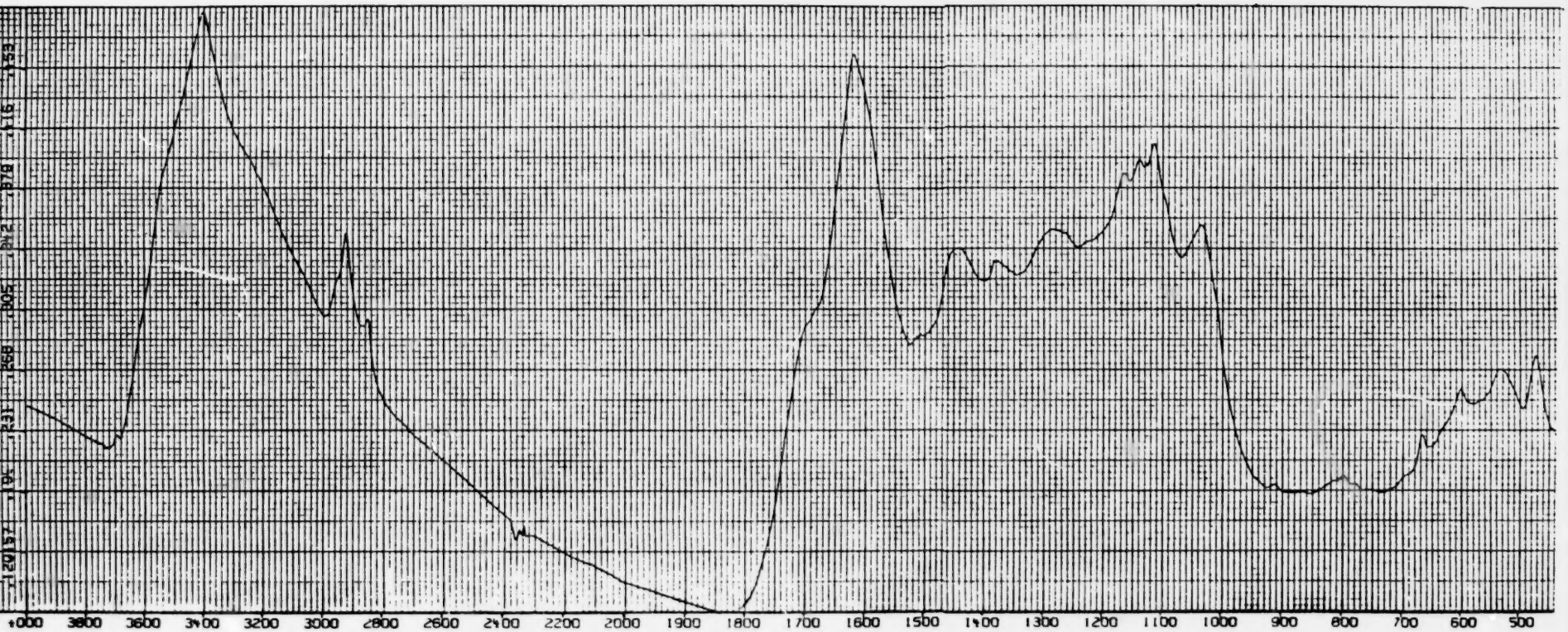

Figure 4: Averaged normalized FTIR spectrum of residue remaining after coal had been heated at 450°C for one hour in the presence of hydrogen.

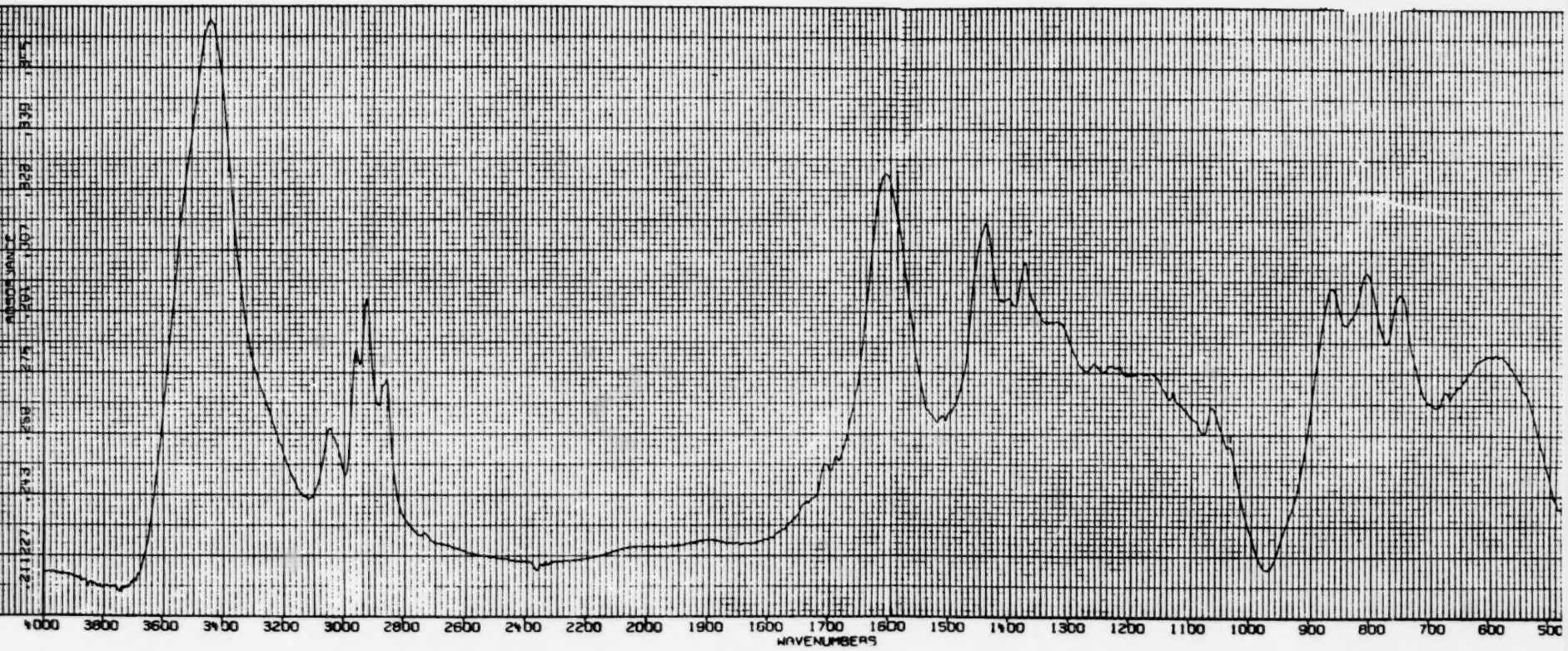

Figure 5: Averaged normalized FTIR spectrum of bitumen coke.

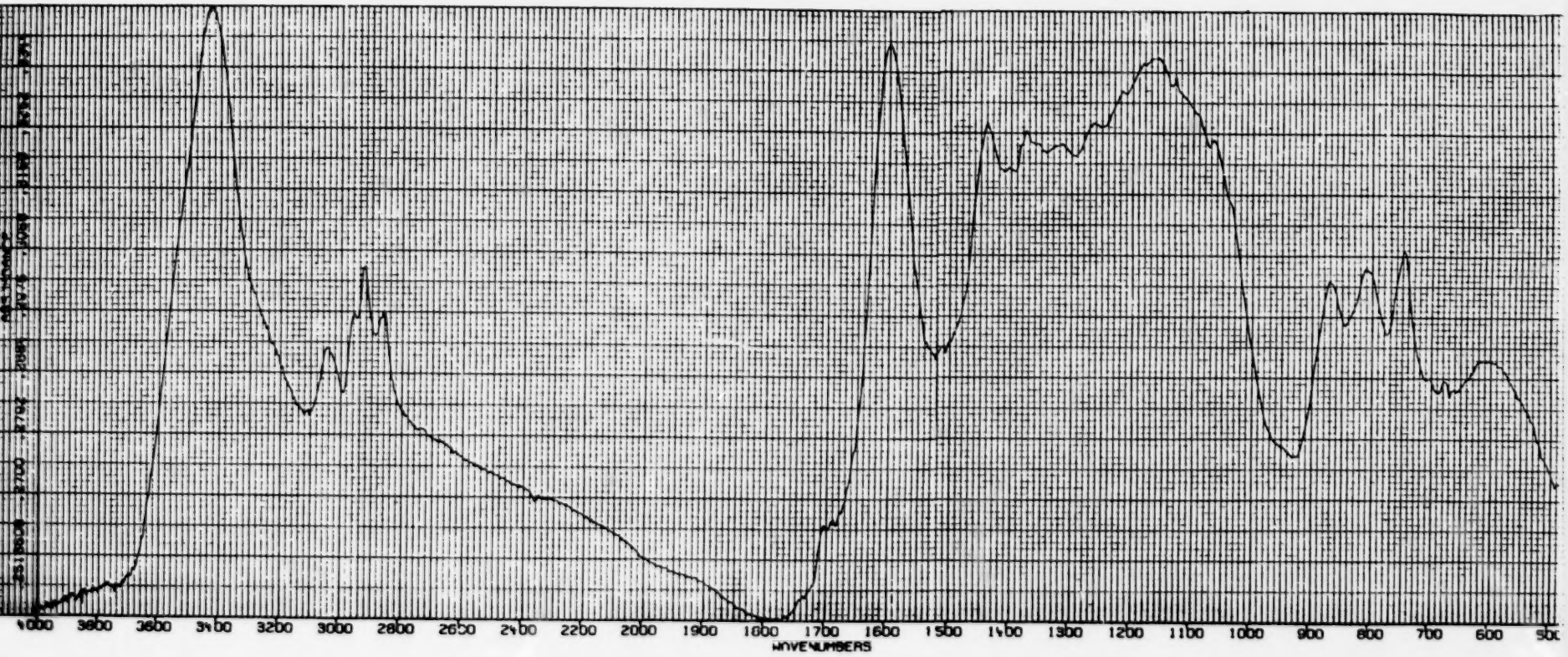

Figure 6: Averaged normalized FTIR spectrum of coal derived liquids coke.

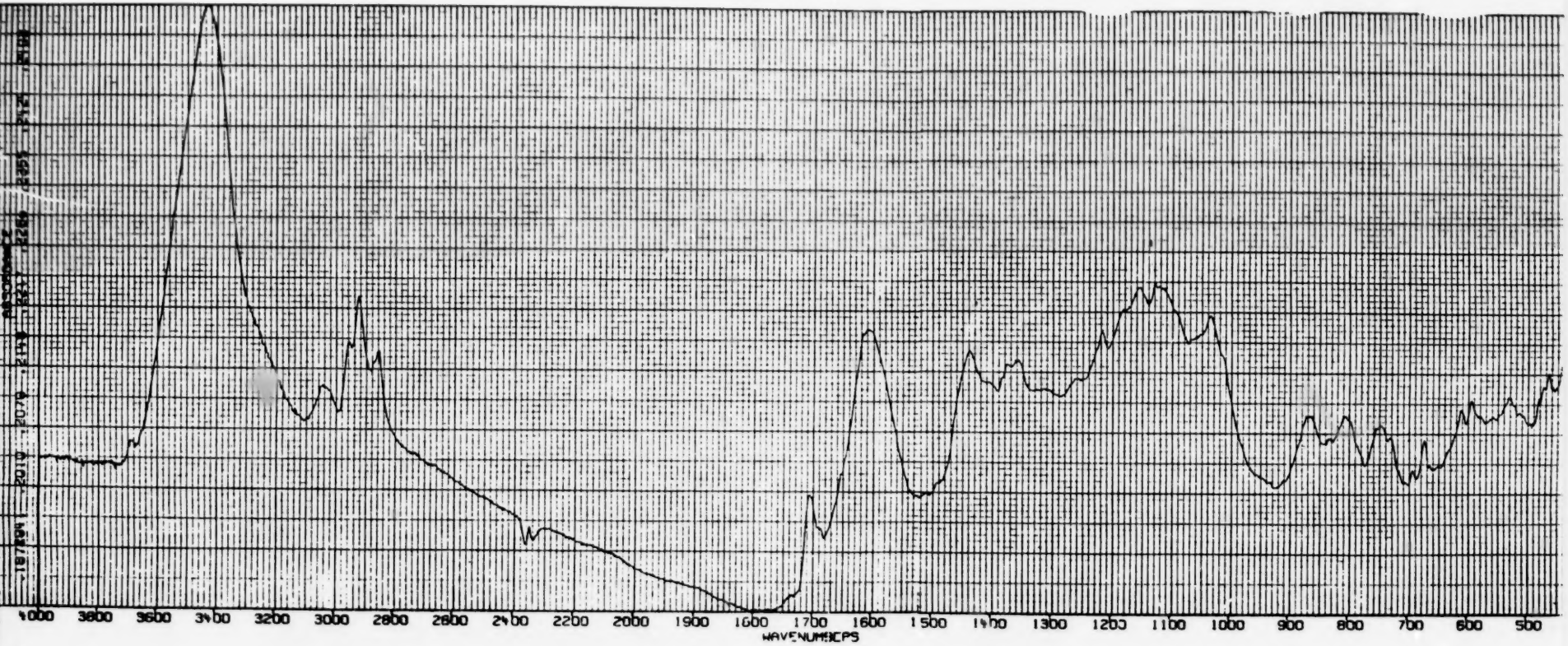

Figure 7: Averaged normalized FTIR spectrum of coprocessing residue.

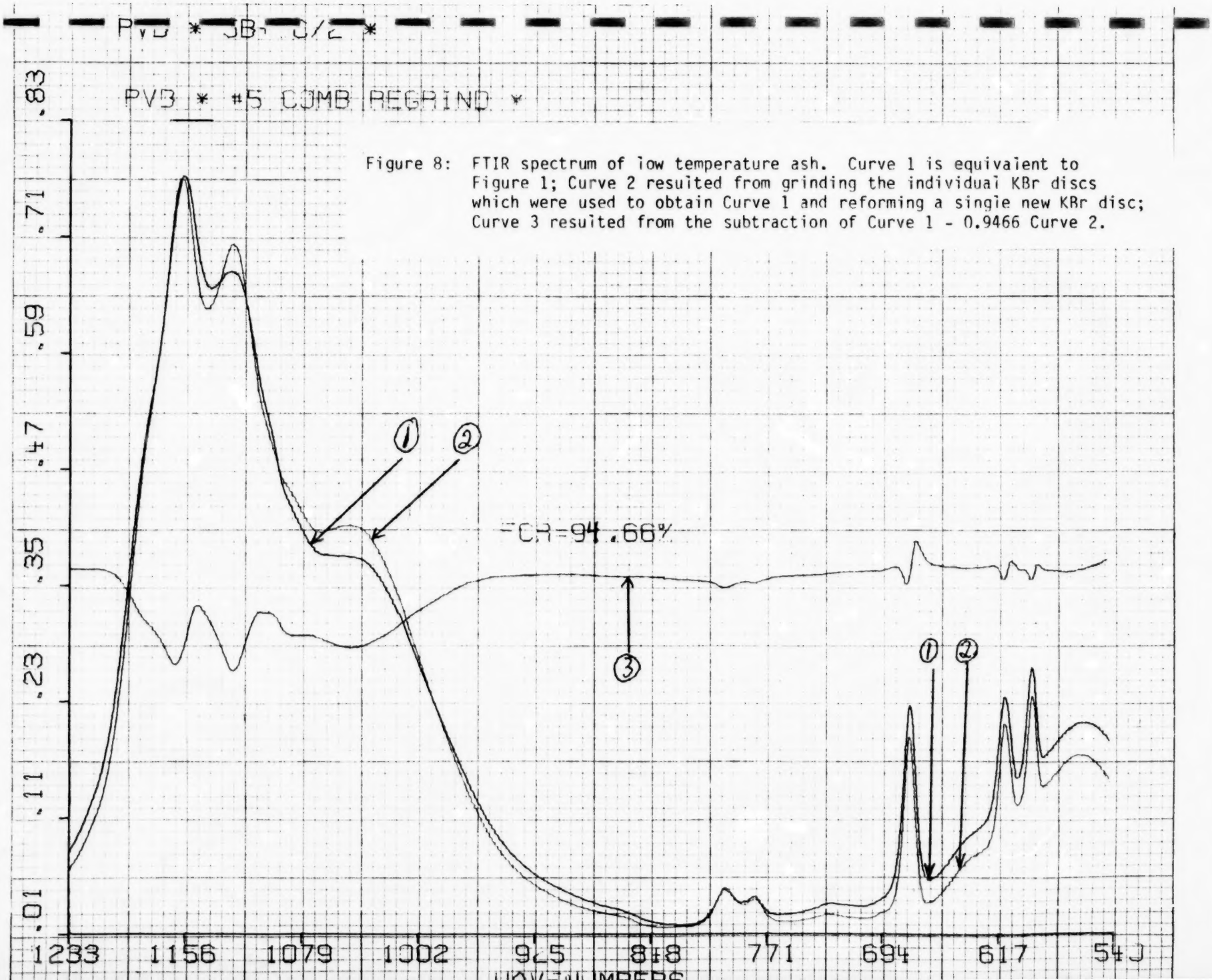

Figure 8: FTIR spectrum of low temperature ash. Curve 1 is equivalent to Figure 1; Curve 2 resulted from grinding the individual KBr discs which were used to obtain Curve 1 and reforming a single new KBr disc; Curve 3 resulted from the subtraction of Curve 1 - 0.9466 Curve 2.

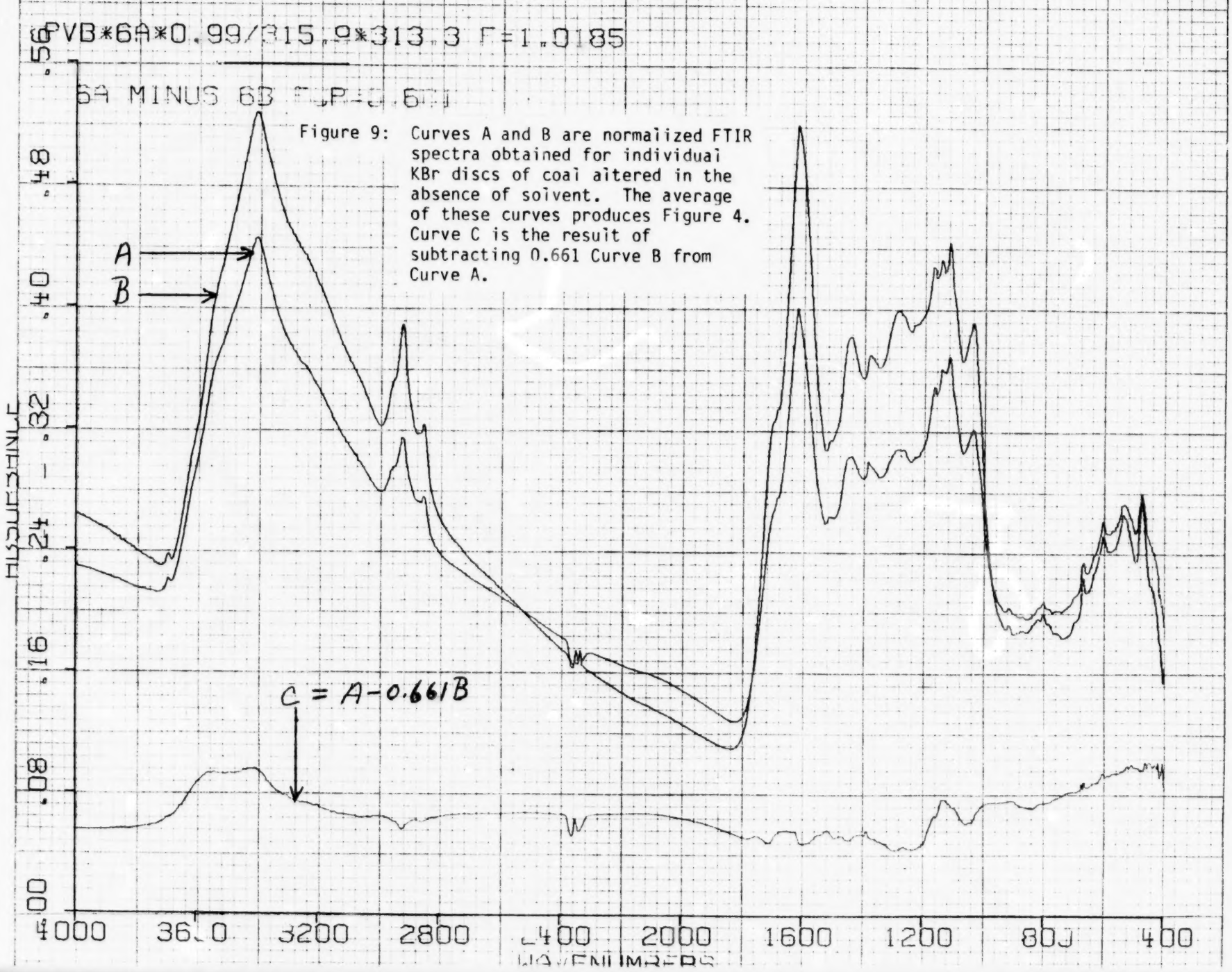

Figure 9: Curves A and B are normalized FTIR spectra obtained for individual KBr discs of coal altered in the absence of solvent. The average of these curves produces Figure 4. Curve C is the result of subtracting 0.661 Curve B from Curve A.

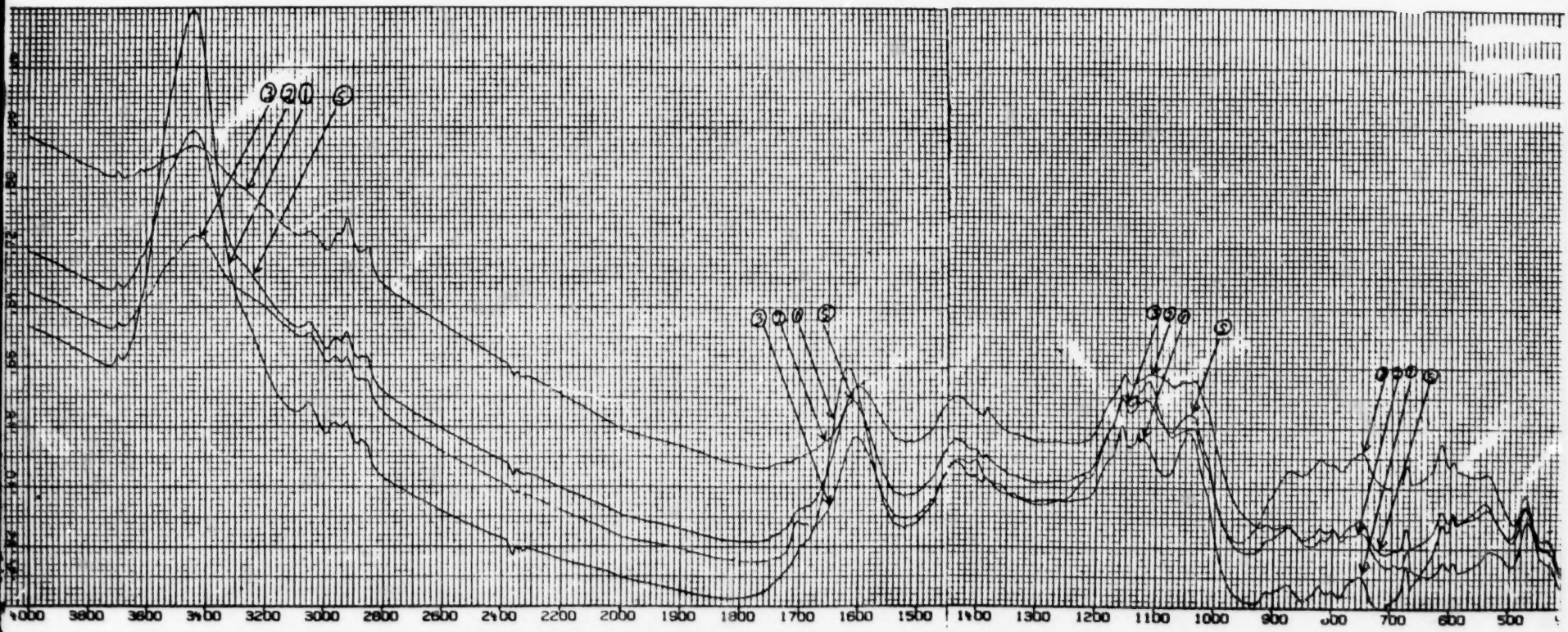

Figure 10: Normalized FTIR spectra of altered coal. Curves 1, 2 and 3 are three different KBr discs prepared from the same coal sample. Curve S is the average of Curves 1, 2 and 3. All curves are on the same absorbance scale.

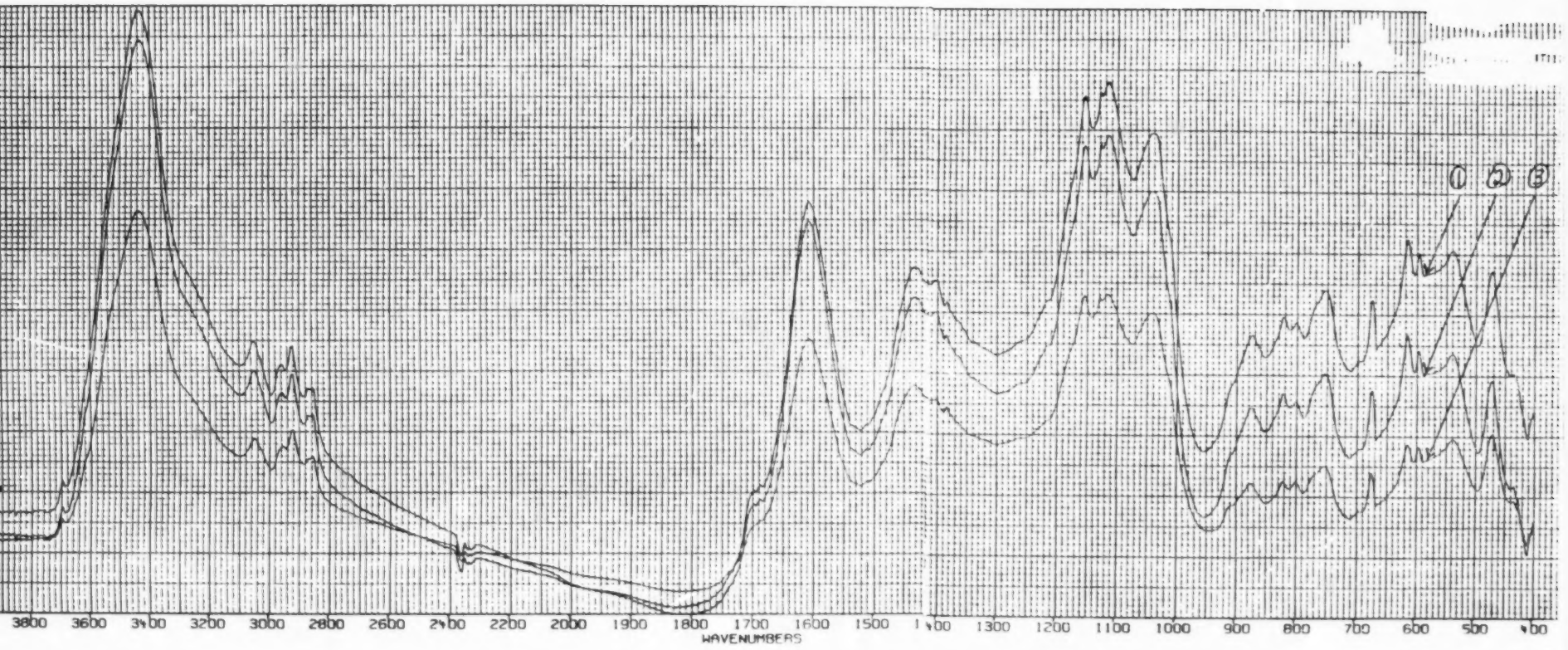

Figure 11: Averaged normalized FTIR spectra of altered coal generated from Curves 1, 2 and 3, Figure 10. Curve 1 was generated by correcting each individual curve for baseline drift followed by application of the coaddition program supplied by Nicolet. Curve 2 was generated by the same program before correcting for baseline drift. Curve 3 was generated by multiplying each individual curve by 0.3333 then adding before correcting for baseline drift. Curve 5, Figure 10 is equivalent to Curve 3. All curves are plotted on the same absorbance scale.

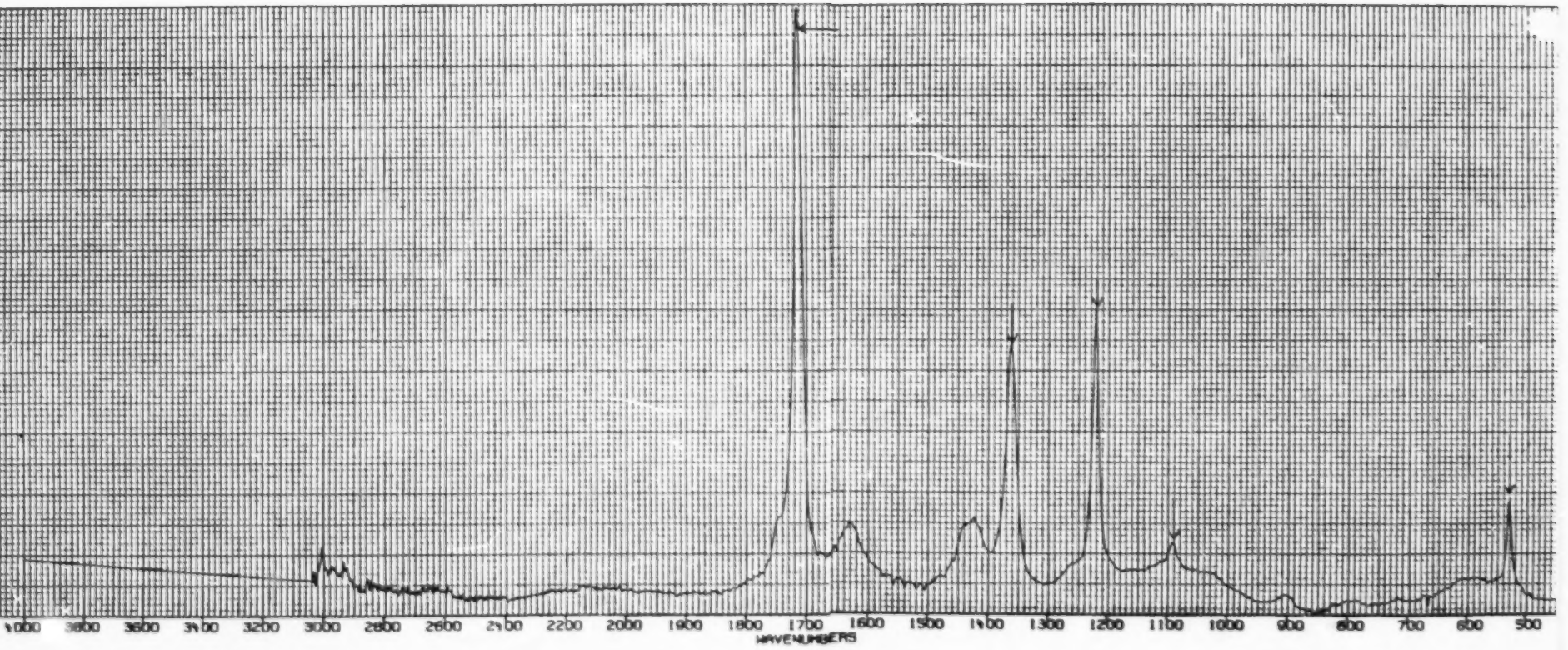

Figure 12: FTIR spectrum of acetone in KBr.

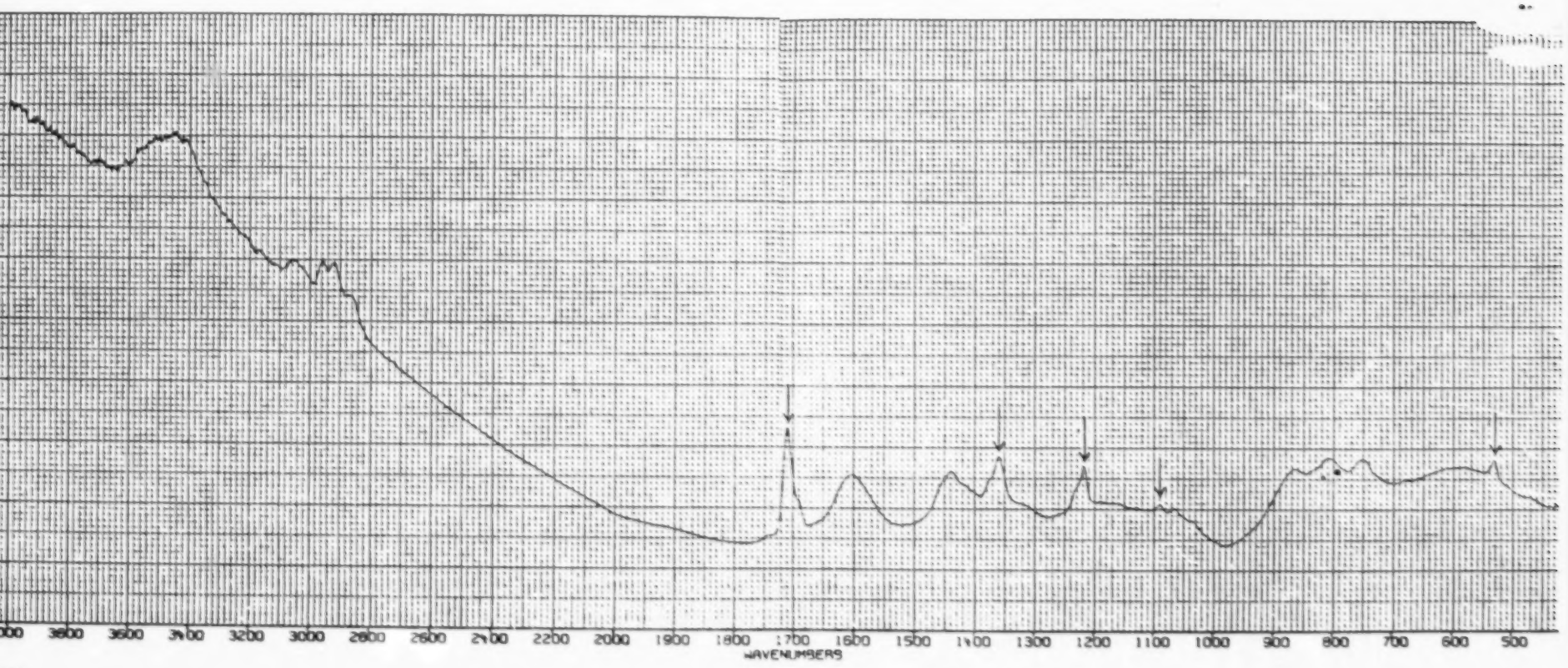

Figure 13: FTIR spectrum of bitumen coke contaminated with acetone. Arrows indicate absorbance bands due to acetone.

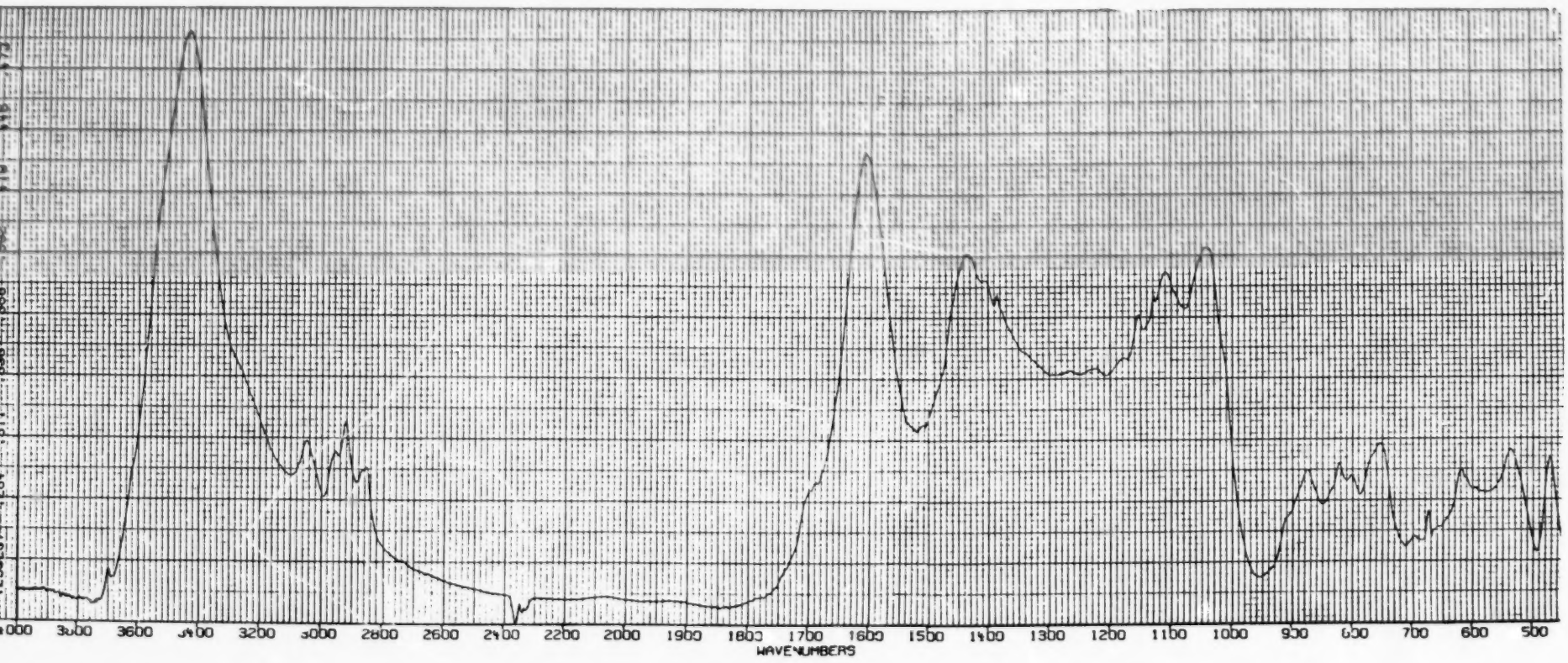

Figure 14: Subtraction of 12.2% averaged normalized ash spectrum from the averaged normalized altered coal spectrum (Figure 2 - 12.2% Figure 1).

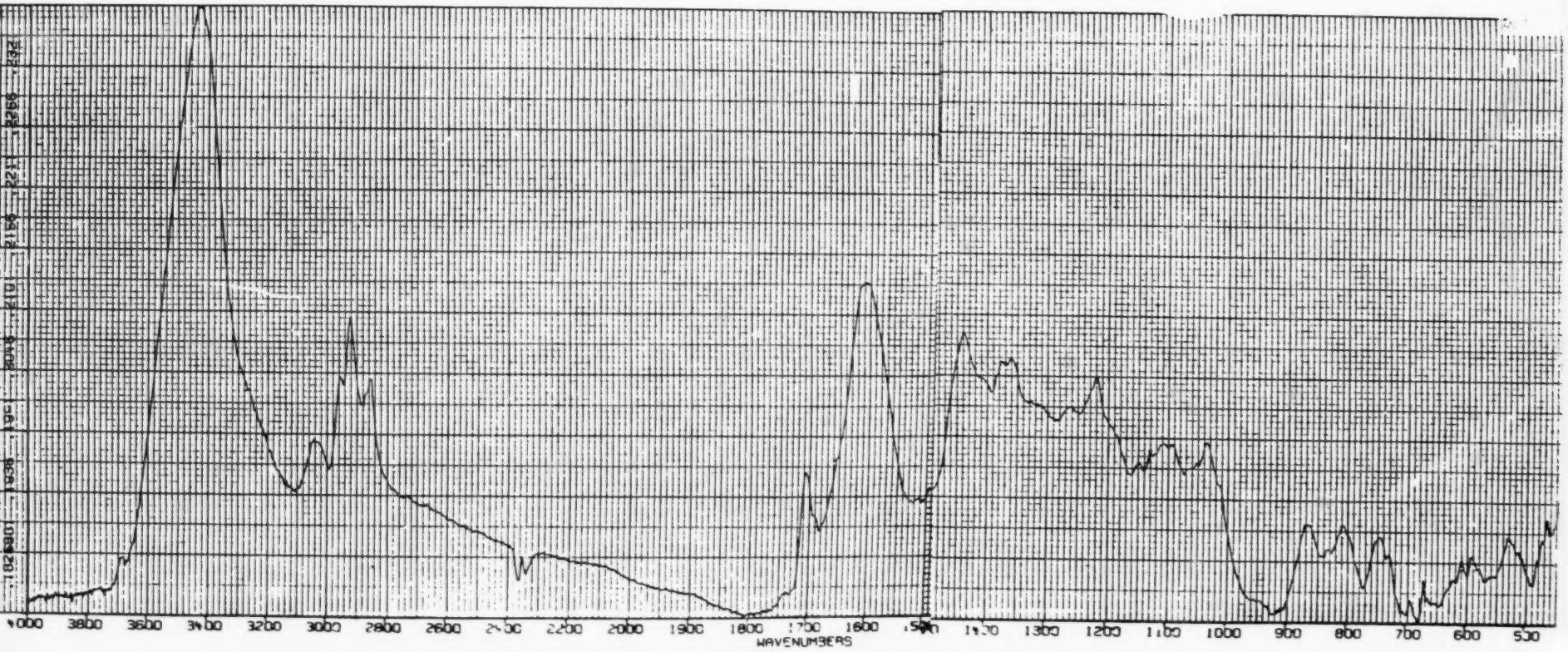

Figure 15: Subtraction of 1.9% averaged normalized ash spectrum from the averaged normalized coprocessing residue spectrum (Figure 7 - 1.9% Figure 1).

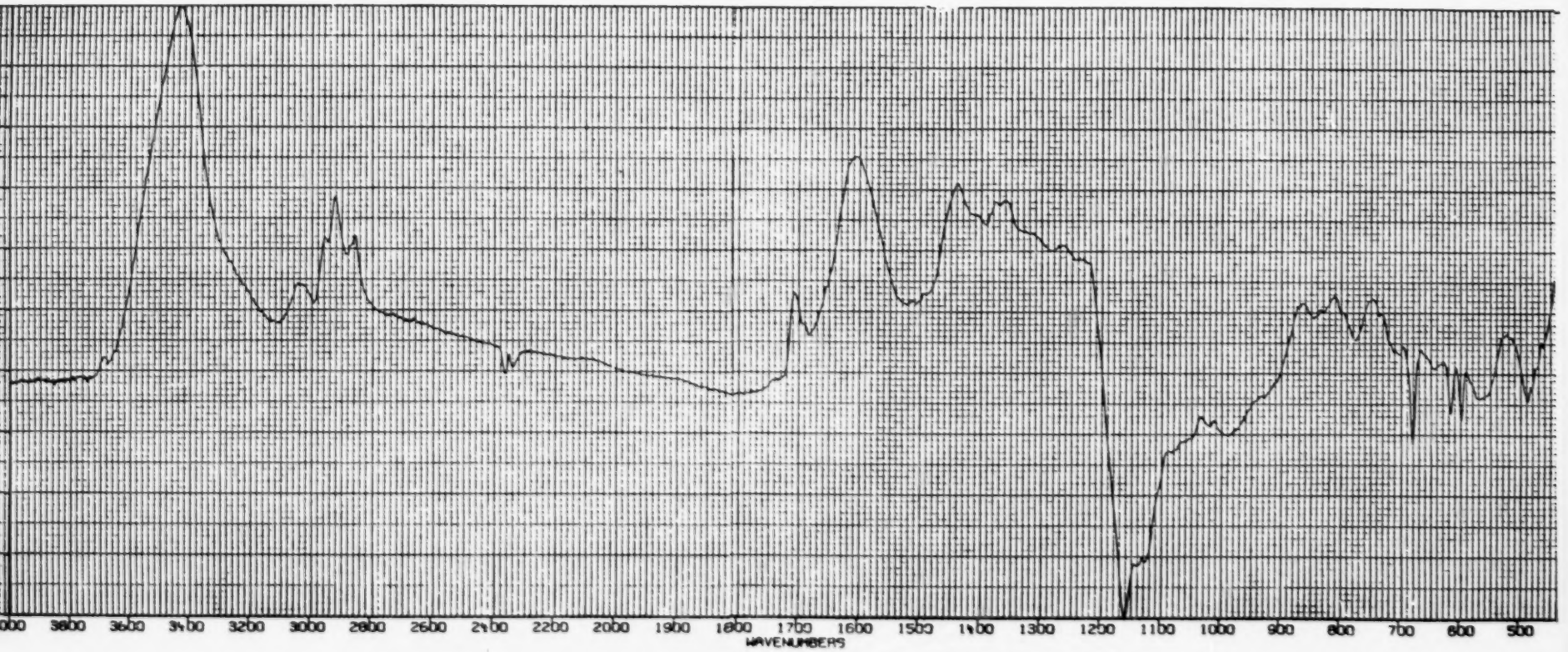

Figure 16: Subtraction of 7.5% averaged normalized ash spectrum from the averaged normalized coprocessing spectrum (Figure 7 - 7.5% Figure 1). Notice the negative absorbance bands attributable to ash. The calculated amount of ash in the coprocessing residue is 7.5%.

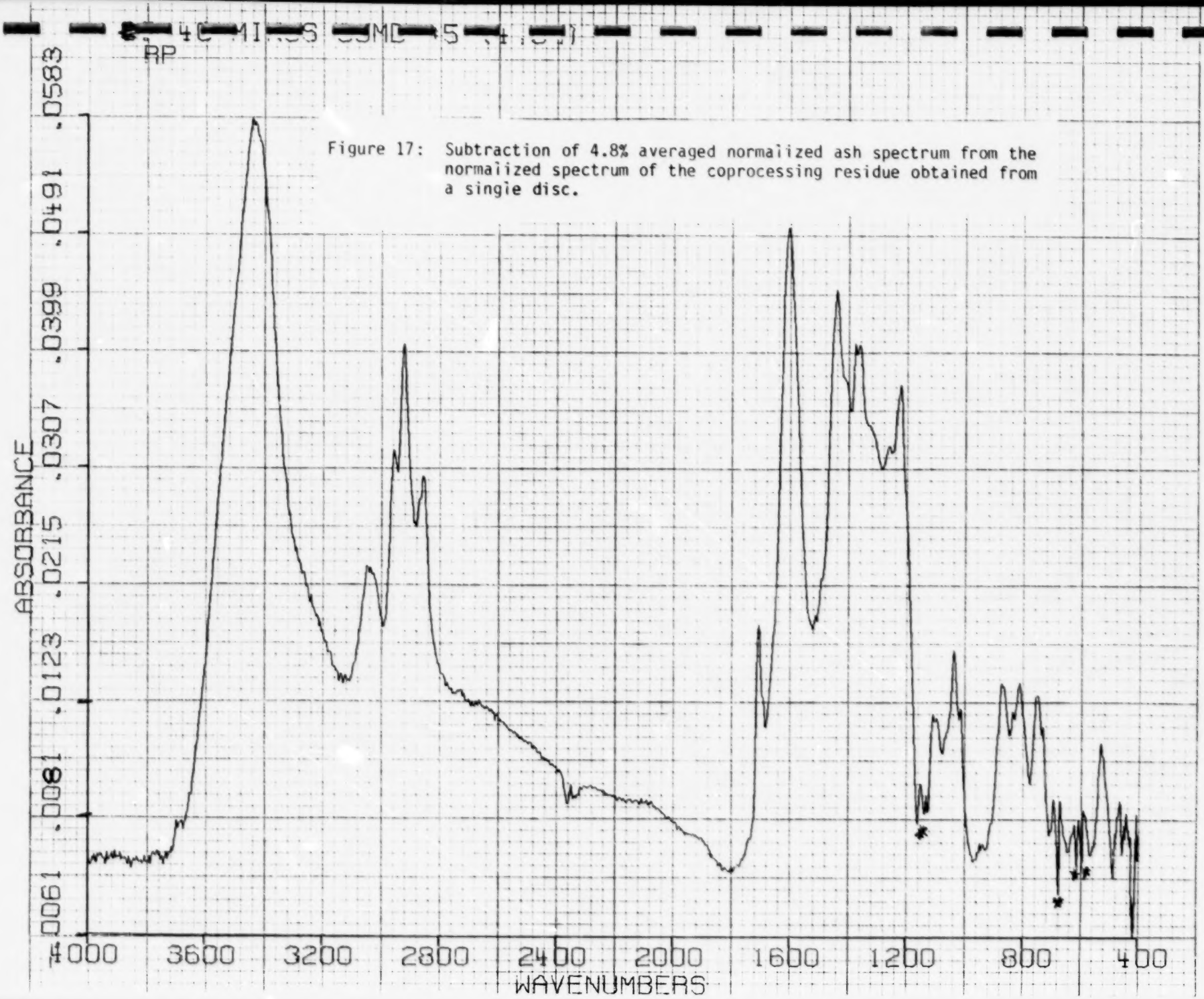

Figure 17: Subtraction of 4.8% averaged normalized ash spectrum from the normalized spectrum of the coprocessing residue obtained from a single disc.

Figure 18: Normalized spectra of the coprocessing residue before baseline correction and absorbance scale expansion. The KBr discs were prepared by grinding the coprocessing residue with KBr in a mortar.

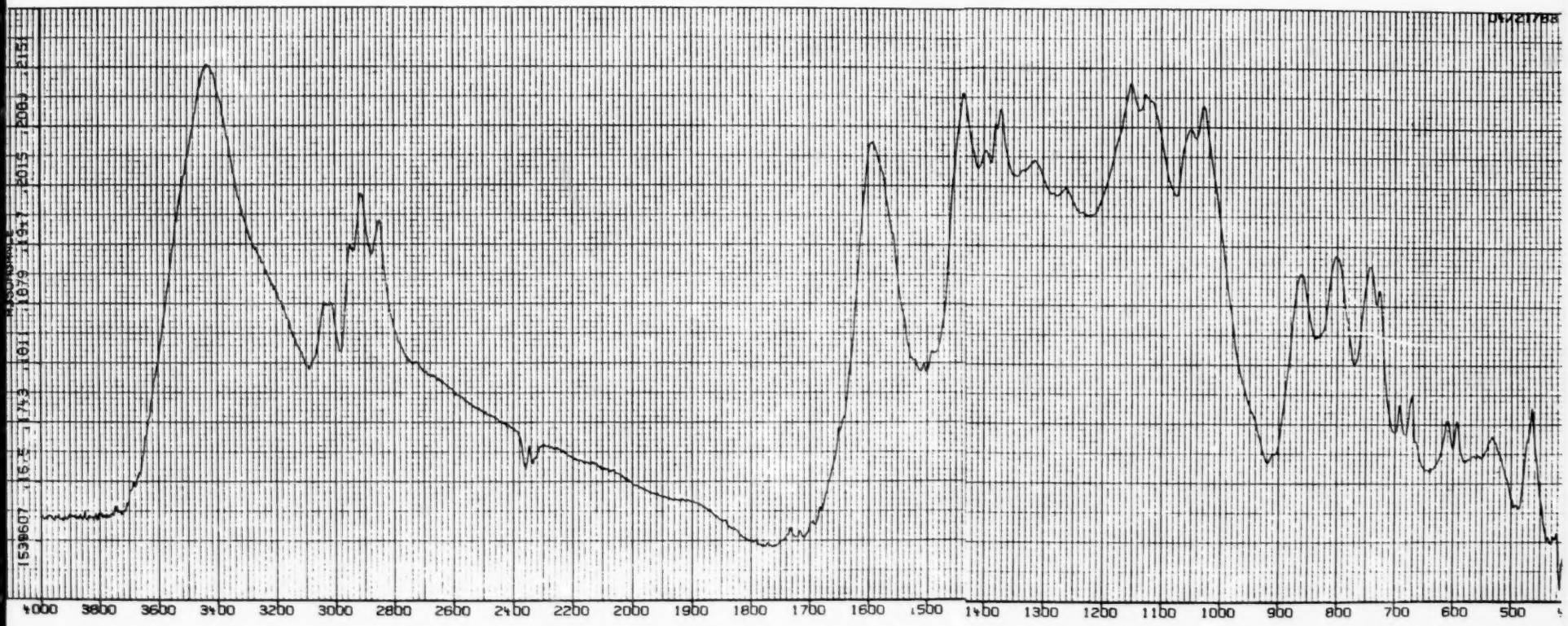

Figure 19: Averaged normalized spectrum of the coprocessing residue obtained after averaging the spectra produced in Figure 18, correcting the baseline and expanding the absorbance scale.

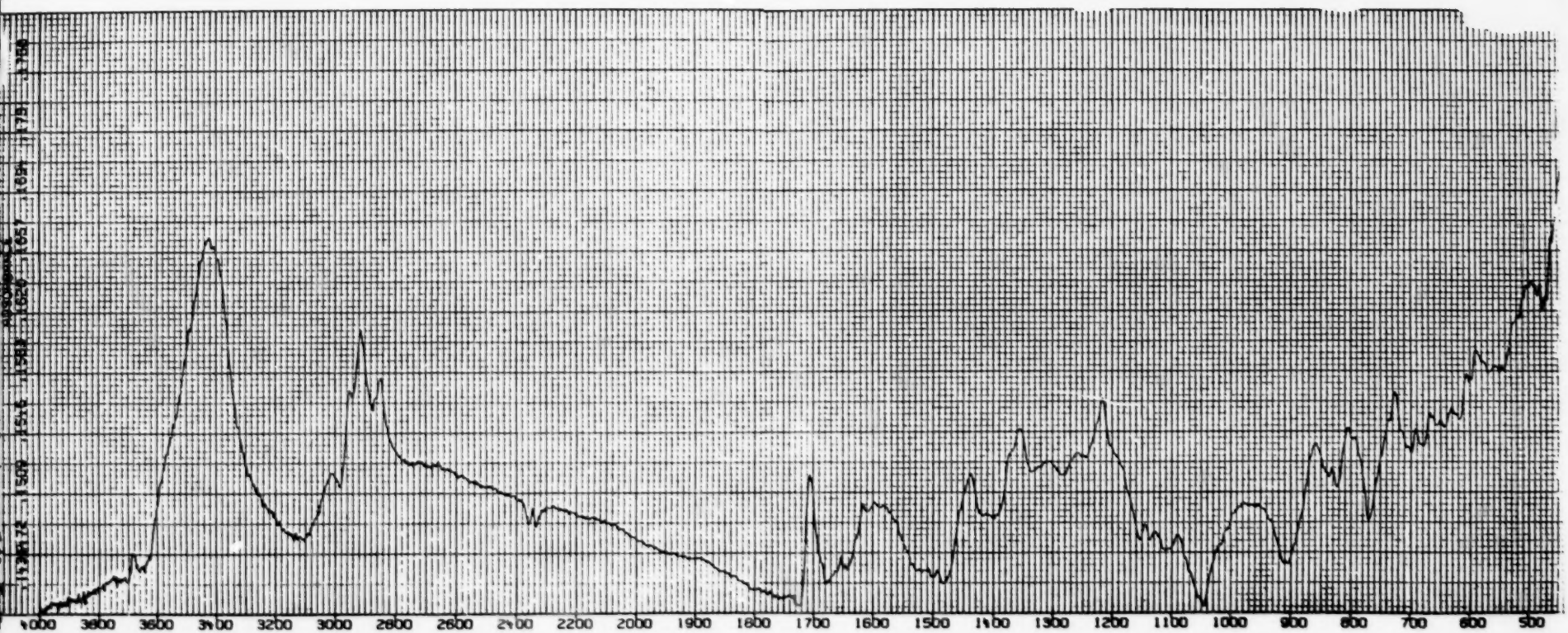

Figure 20: Subtraction of 13% of the averaged normalized altered coal spectrum from the averaged normalized coprocessing residue spectrum (Figure 7 - 13% of Figure 2).

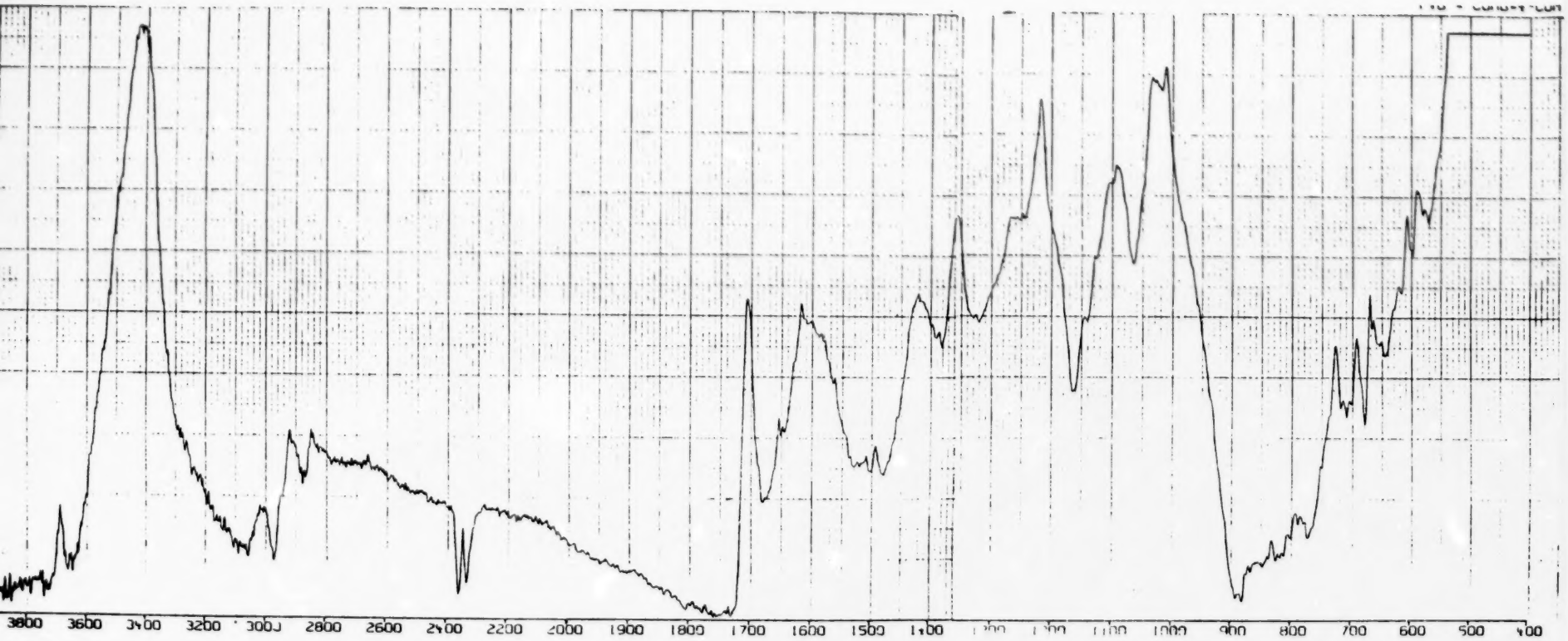

Figure 21: Subtraction of 24% of the averaged normaiized spectrum of bitumen coke from the averaged normaiized spectrum of the coprocessing residue (Figure 7 - 24% Figure 5).

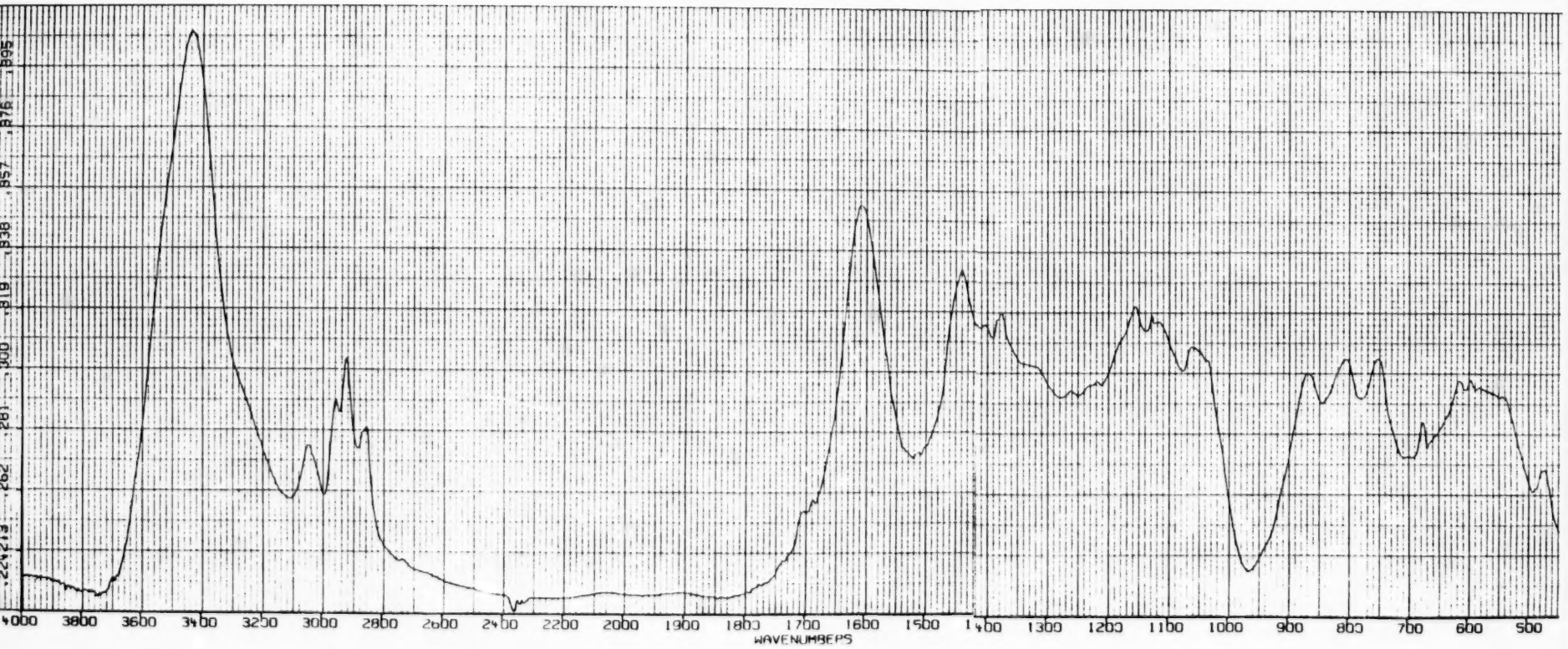

Figure 22: Spectrum synthesized by adding 25% of the altered coal spectrum (Figure 2) and 75% of the bitumen coke spectrum (Figure 5).

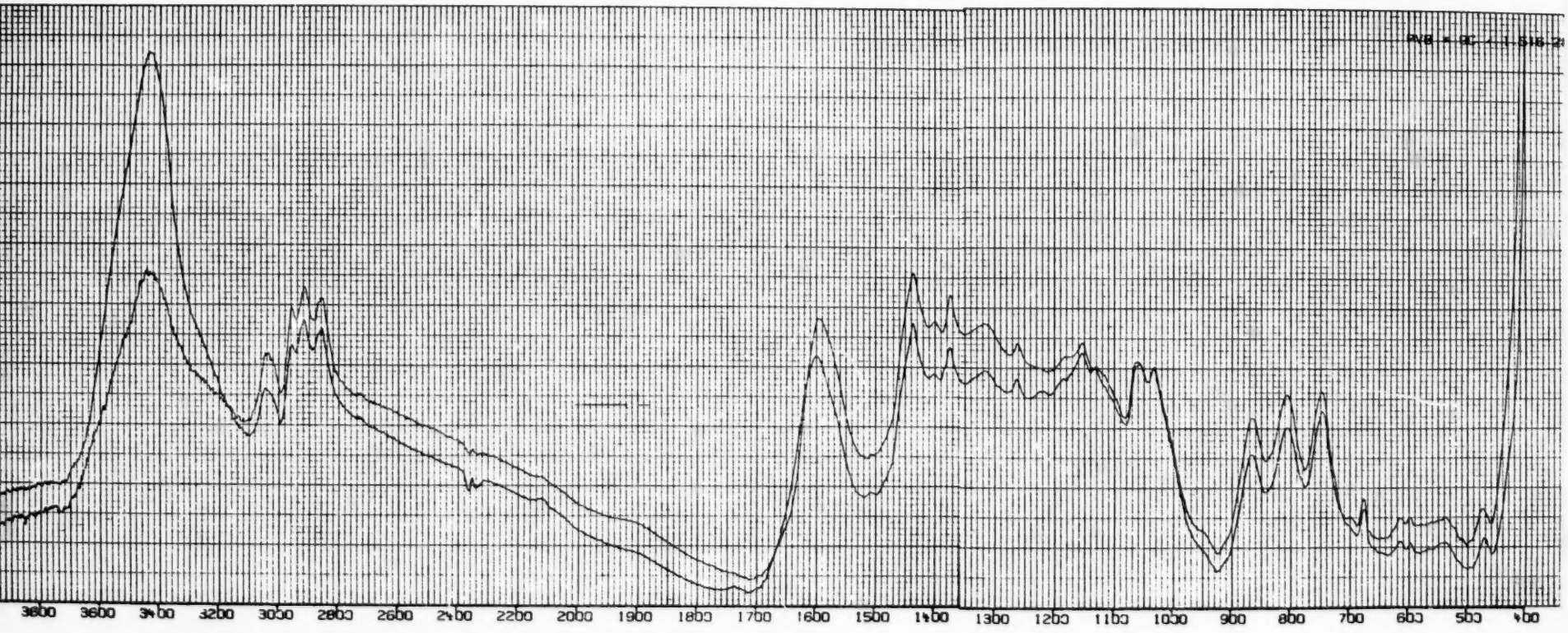

Figure 23: Spectra of a physical mixture made up of 25% altered coal and 75% bitumen coke. The spectra in Figures 22 and 23 should be identical.

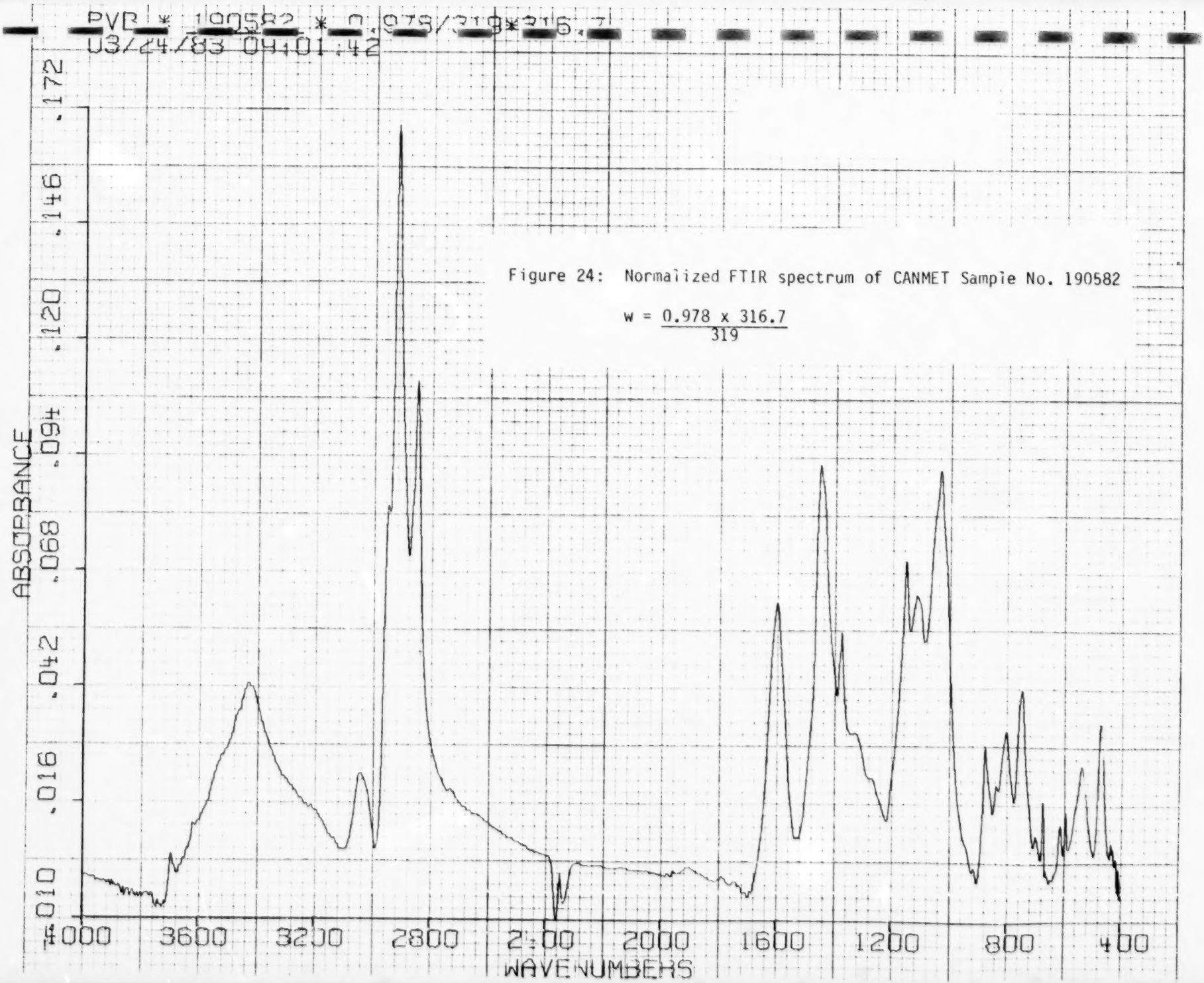

Figure 24: Normalized FTIR spectrum of CANMET Sample No. 190582

$$w = \frac{0.978 \times 316.7}{319}$$

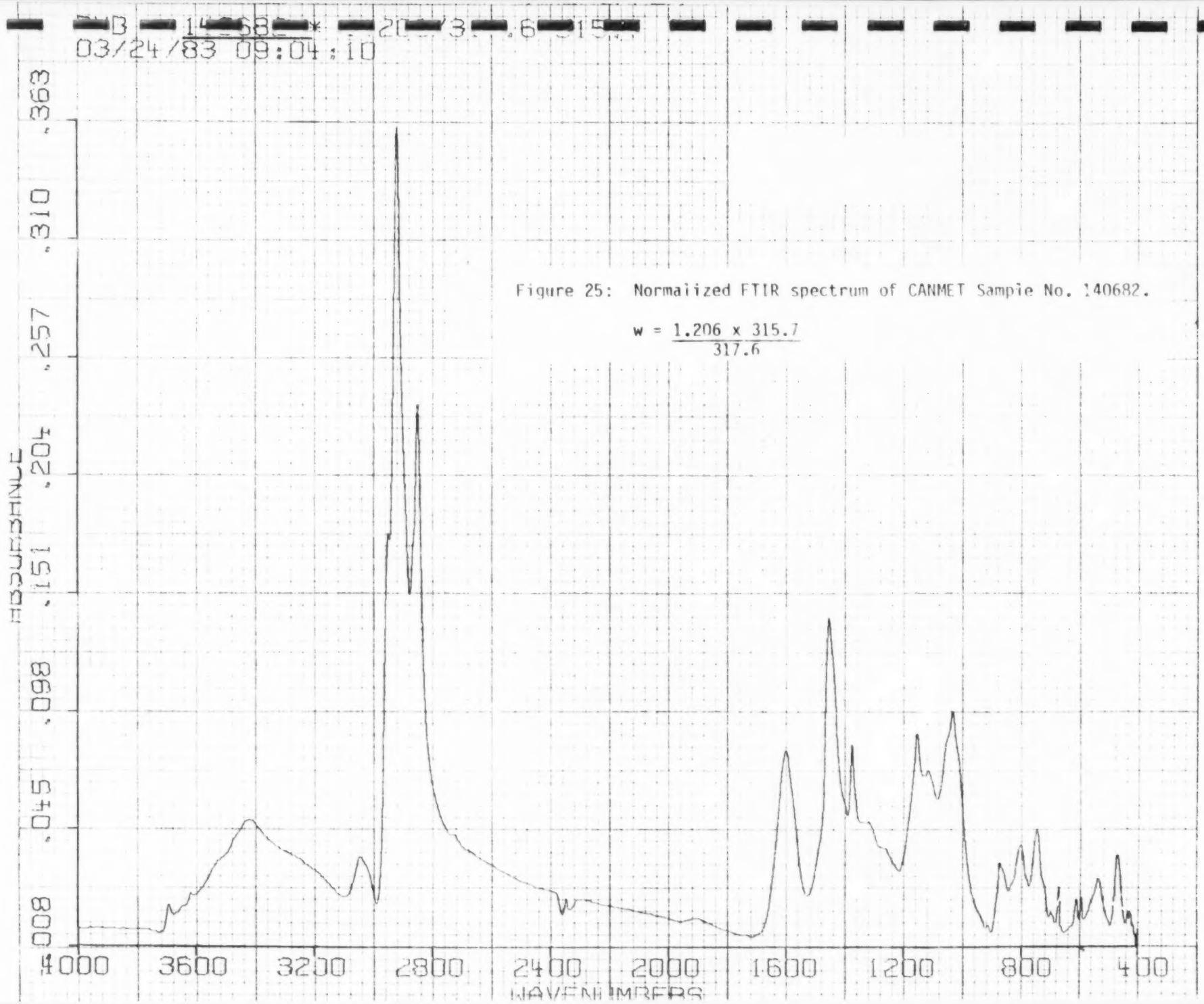

Figure 25: Normalized FTIR spectrum of CANMET Sample No. 140682.

$$w = \frac{1.206 \times 315.7}{317.6}$$

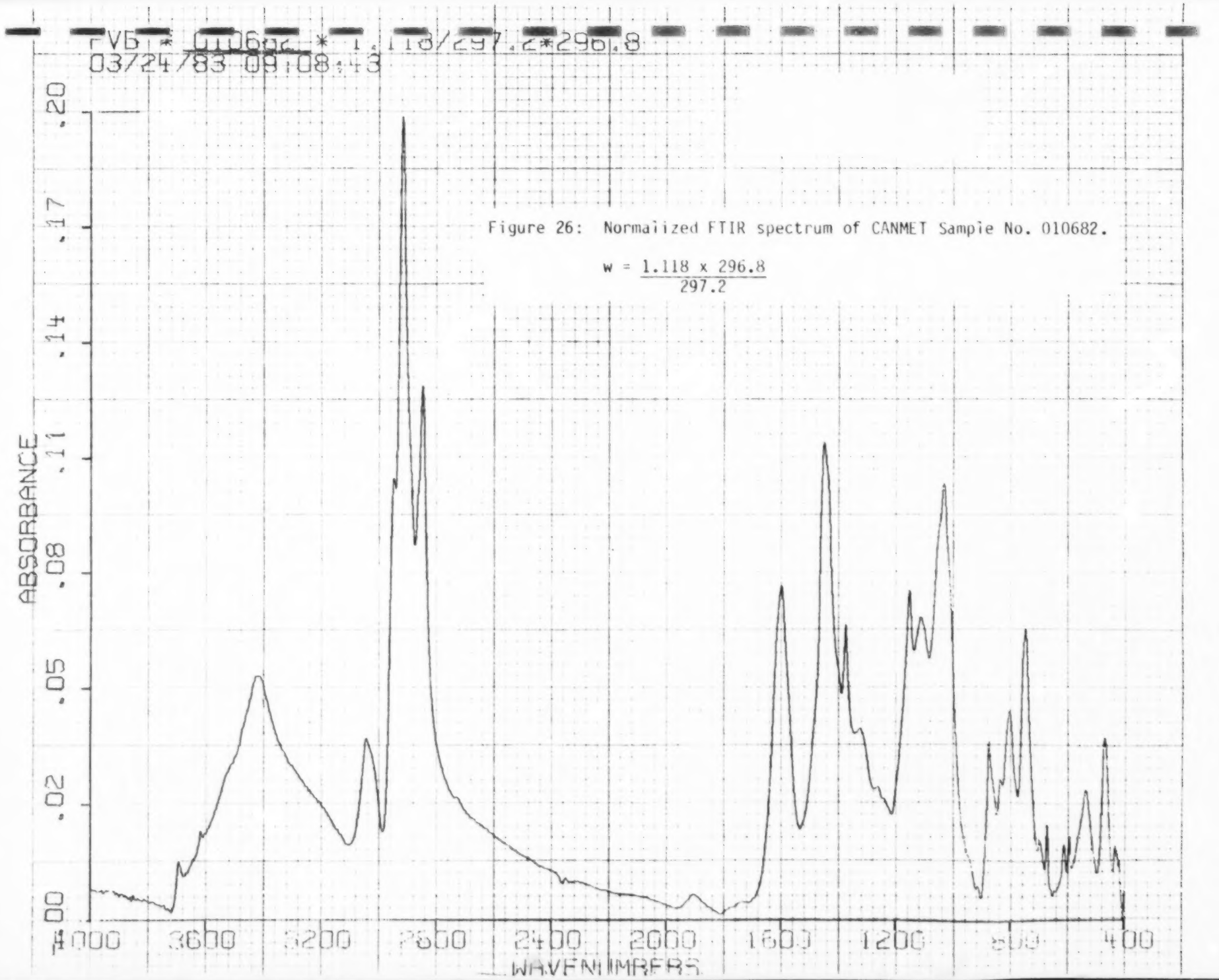

Figure 26: Normalized FTIR spectrum of CANMET Sample No. 010682.

$$w = \frac{1.118 \times 296.8}{297.2}$$

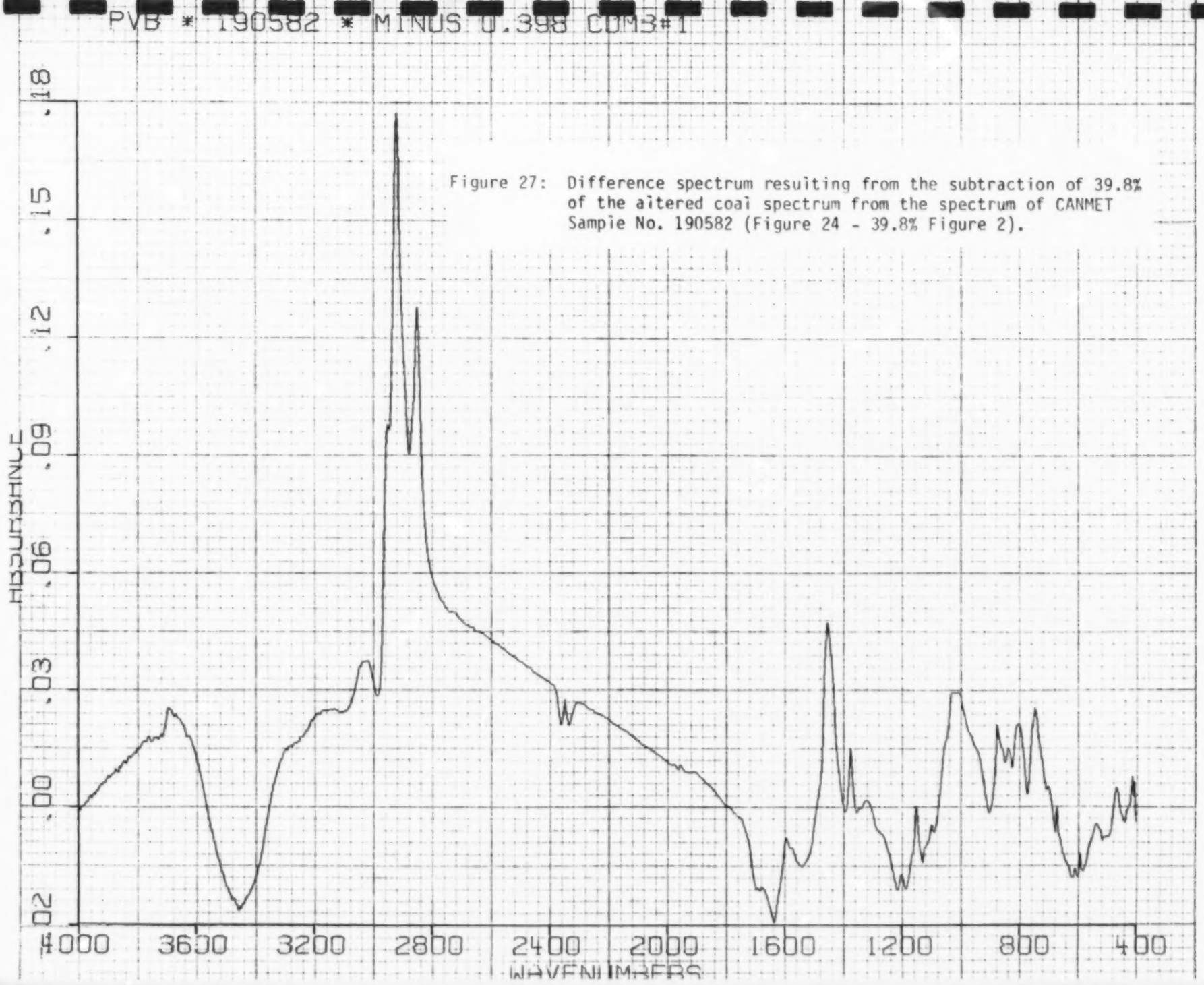

Figure 27: Difference spectrum resulting from the subtraction of 39.8% of the altered coal spectrum from the spectrum of CANMET Sample No. 190582 (Figure 24 - 39.8% Figure 2).

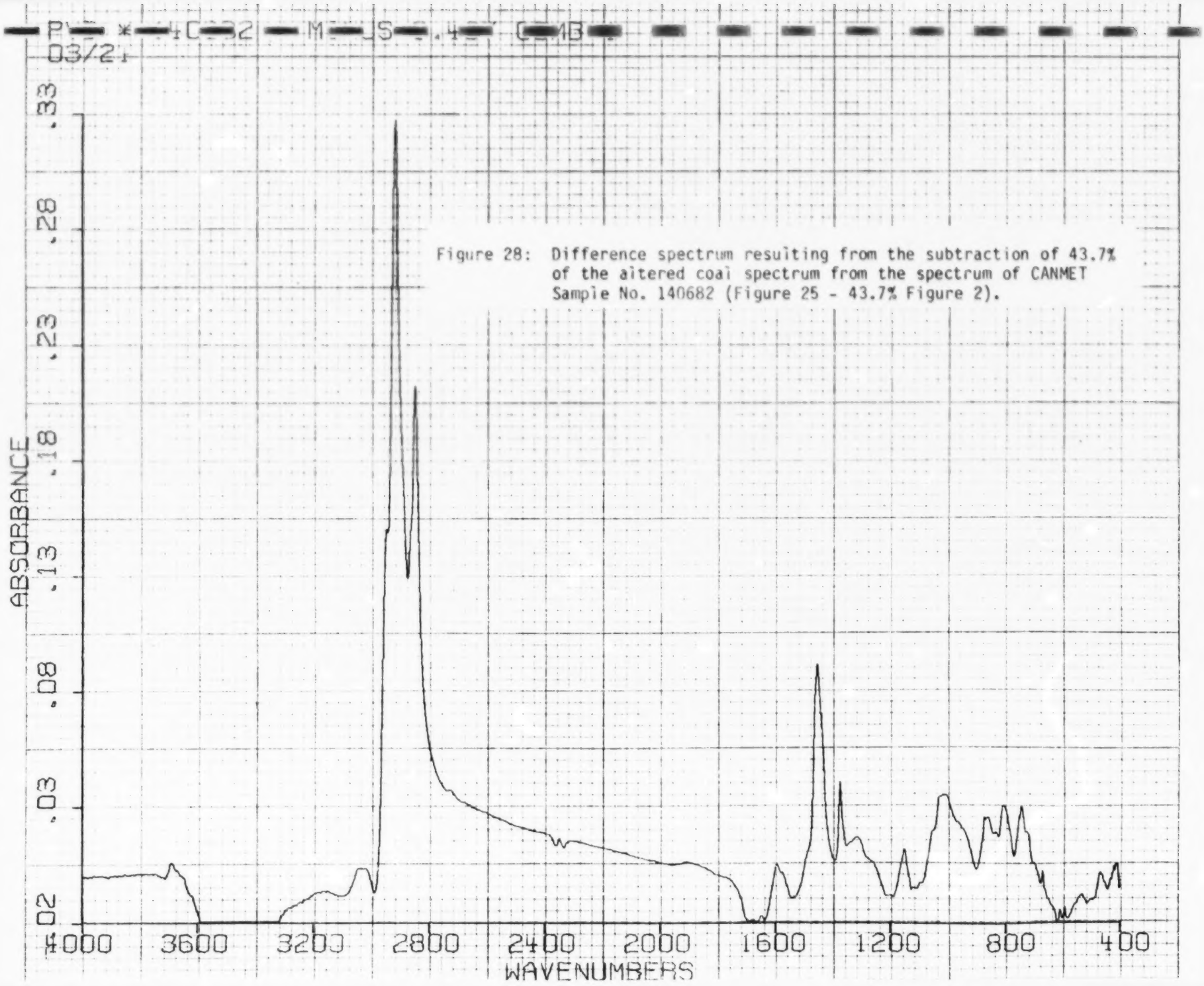

Figure 28: Difference spectrum resulting from the subtraction of 43.7% of the altered coal spectrum from the spectrum of CANMET Sample No. 140682 (Figure 25 - 43.7% Figure 2).

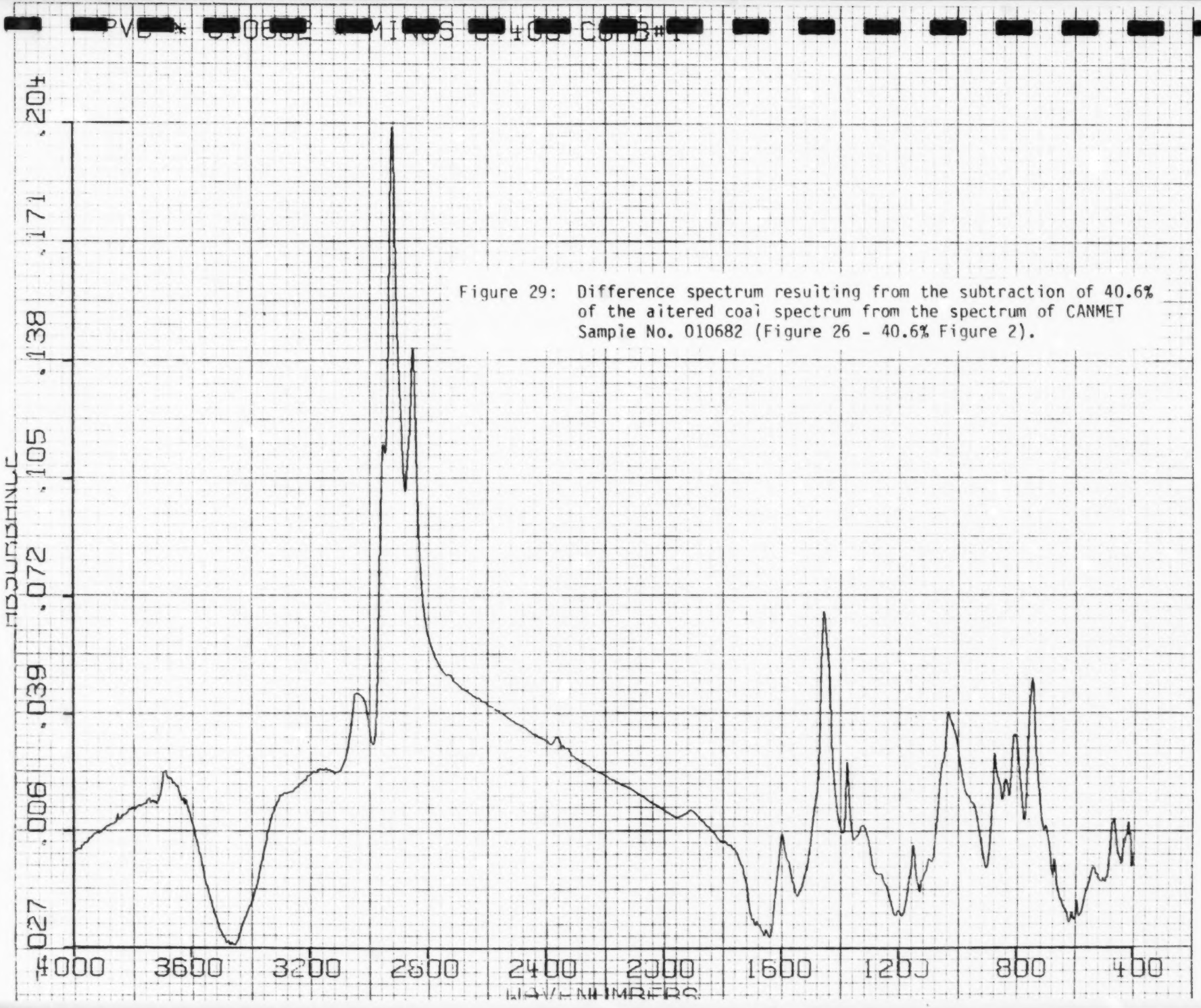

Figure 29: Difference spectrum resulting from the subtraction of 40.6% of the altered coal spectrum from the spectrum of CANMET Sample No. 010682 (Figure 26 - 40.6% Figure 2).

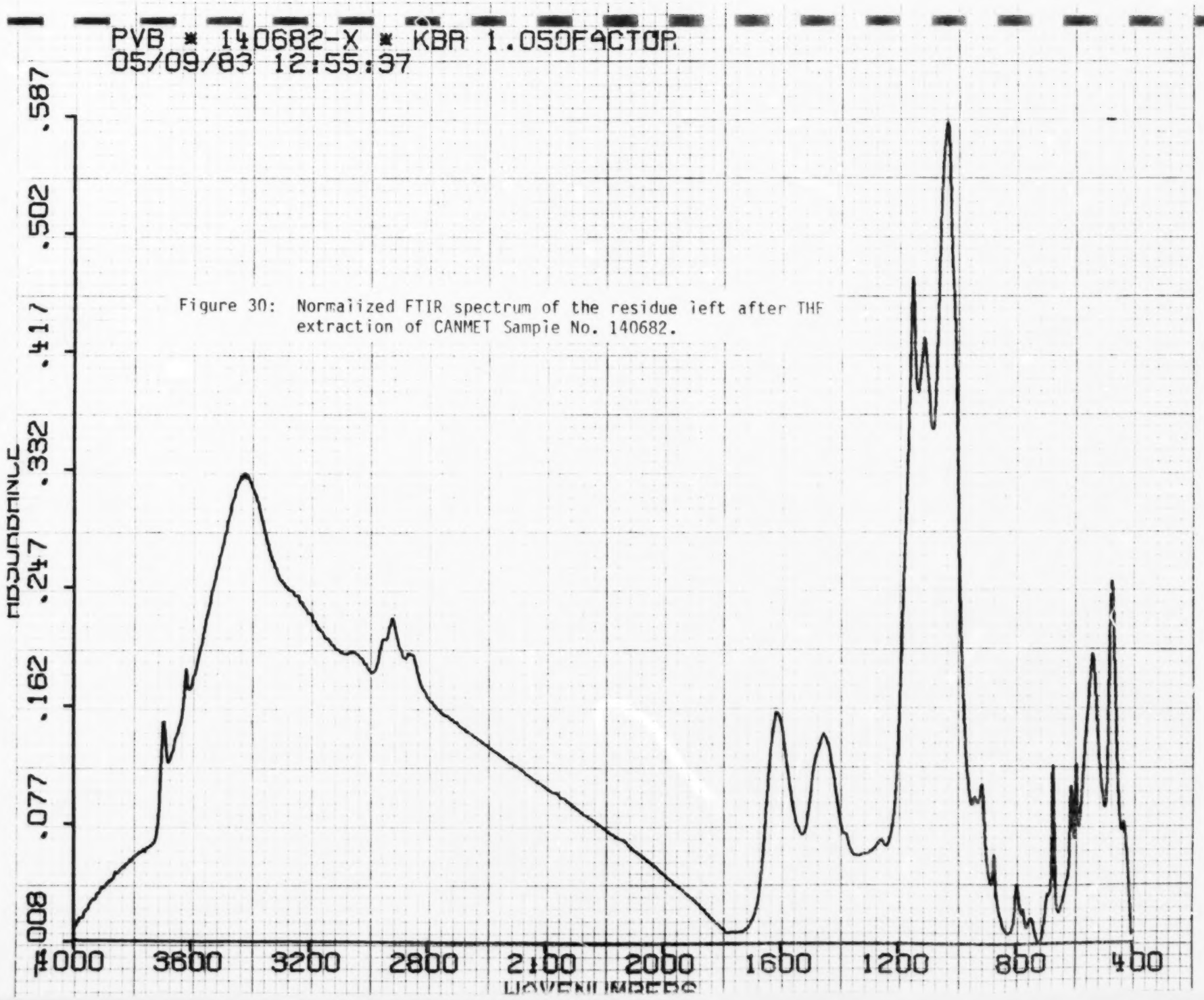

Figure 30: Normalized FTIR spectrum of the residue left after THF extraction of CANMET Sample No. 140682.

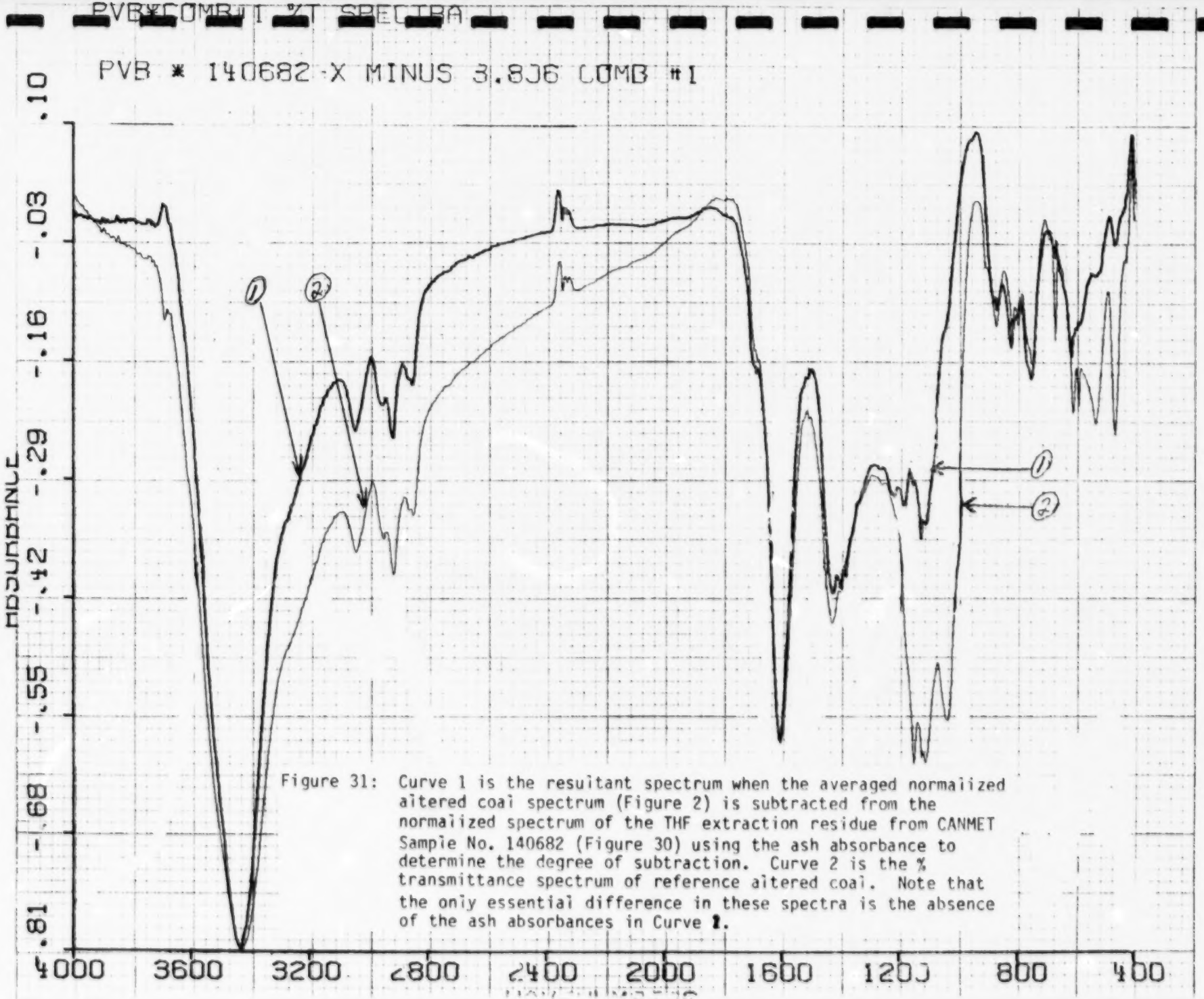

Figure 31: Curve 1 is the resultant spectrum when the averaged normalized altered coal spectrum (Figure 2) is subtracted from the normalized spectrum of the THF extraction residue from CANMET Sample No. 140682 (Figure 30) using the ash absorbance to determine the degree of subtraction. Curve 2 is the % transmittance spectrum of reference altered coal. Note that the only essential difference in these spectra is the absence of the ash absorbances in Curve 1.

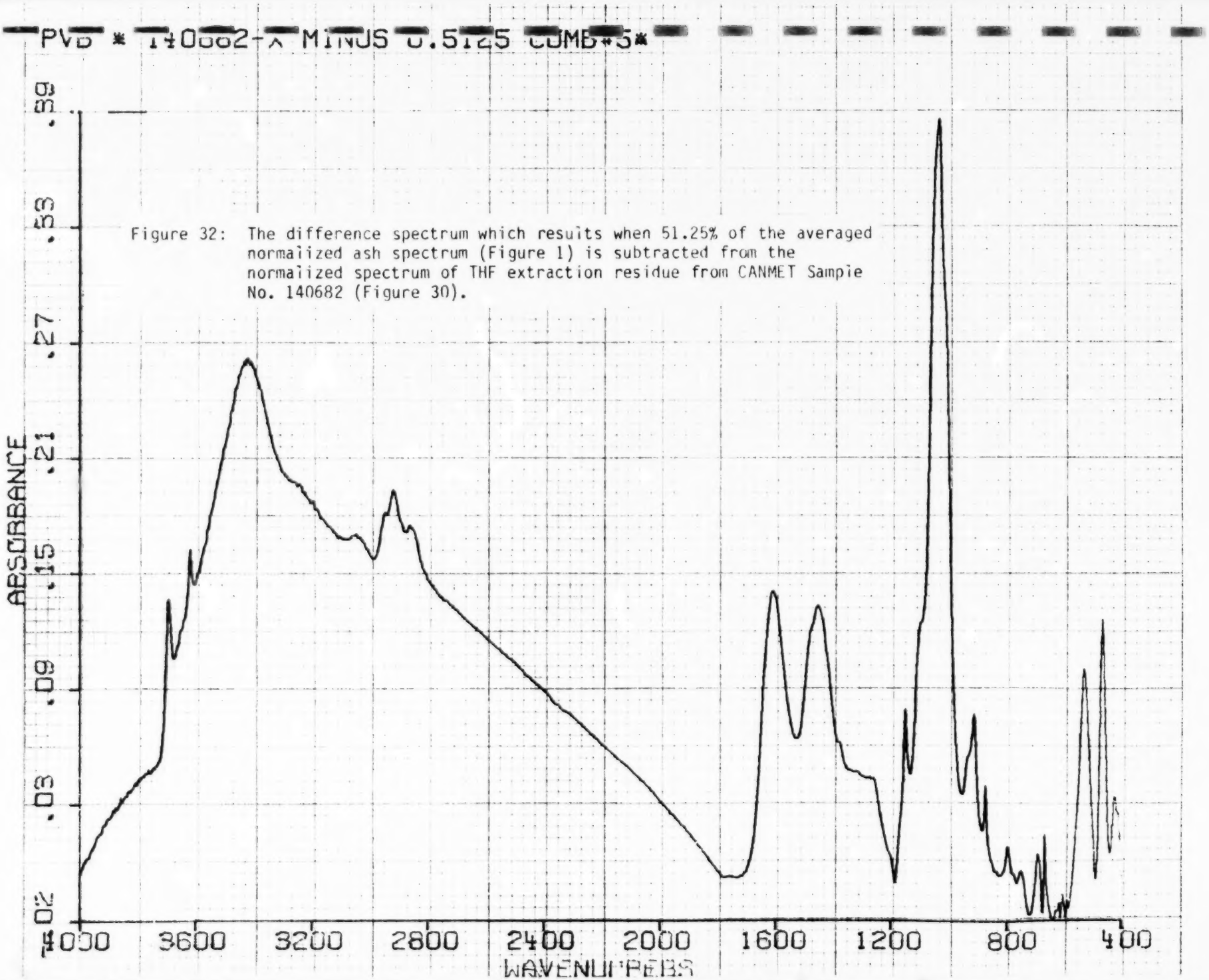

Figure 32: The difference spectrum which results when 51.25% of the averaged normalized ash spectrum (Figure 1) is subtracted from the normalized spectrum of THF extraction residue from CANMET Sample No. 140682 (Figure 30).

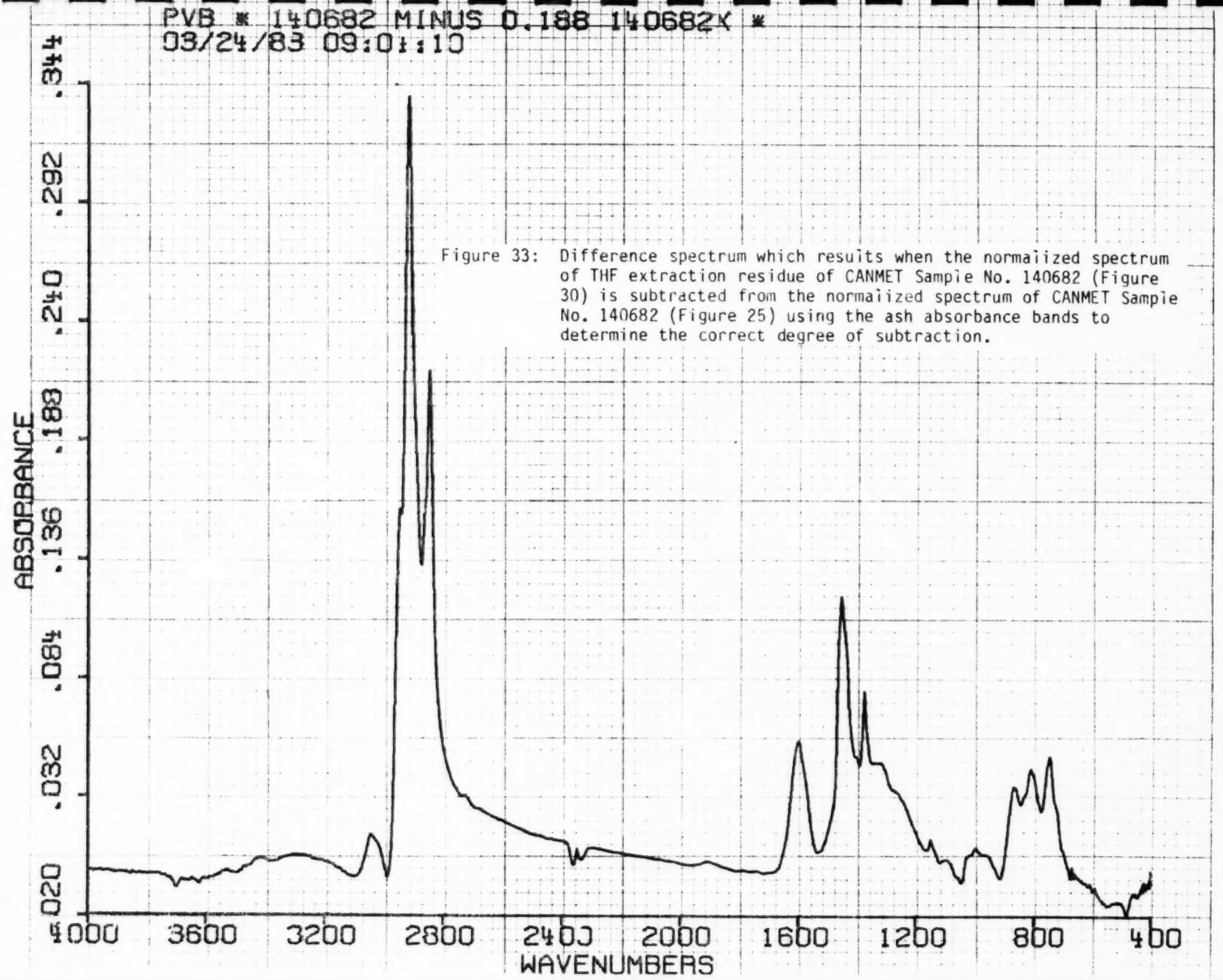

Figure 33: Difference spectrum which results when the normalized spectrum of THF extraction residue of CANMET Sample No. 140682 (Figure 30) is subtracted from the normalized spectrum of CANMET Sample No. 140682 (Figure 25) using the ash absorbance bands to determine the correct degree of subtraction.

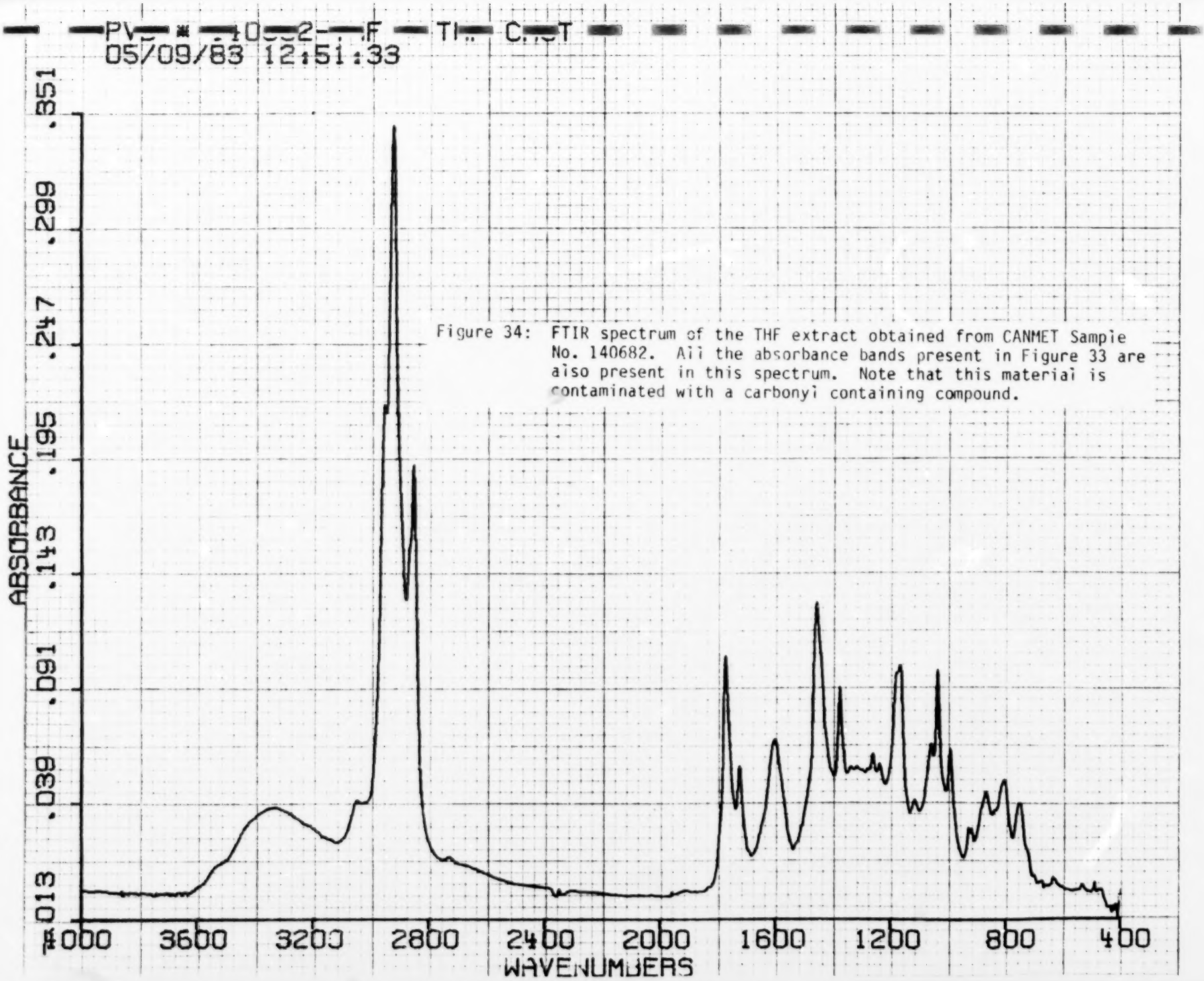

Figure 34: FTIR spectrum of the THF extract obtained from CANMET Sample No. 140682. All the absorbance bands present in Figure 33 are also present in this spectrum. Note that this material is contaminated with a carbonyl containing compound.